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(54) METHOD FOR PRODUCING LAMINAR LITHIUM NICKEL MANGANESE
COMPLEX OXIDE POWDER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing a laminar lithium nickel manganese complex oxide powder, which has a high bulk density and is preferably used for the positive electrode active substance of lithium secondary cell.

SOLUTION: A compression shear stress is applied to a laminar lithium nickel manganese complex oxide powder with a nickel atom [Ni] and a manganese atom [Mn] in a weight ratio [Ni/Mn] of 0.7 to 90 to obtain the product laminar lithium nickel manganese complex oxide powder.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles characterized by performing after treatment which applies compression shearing stress to the stratified lithium nickel manganese multiple oxide fine particles which have the mole ratio [nickel/Mn] of a nickel atom [nickel] and a manganese atom [Mn] in the range of 0.7-9.0.

[Claim 2] The manufacture approach of stratified lithium nickel manganese multiple oxide fine particles according to claim 1 that stratified lithium nickel manganese multiple oxide fine particles are the multiple oxides expressed with the following general formula (I).

[Formula 1]

$Lix Niy Mnz Q(1-Y-Z).O_2$ (I)

x are the number of $0 < x \leq 1.2$ among [type (I), y and z are $0.7 \leq y/z \leq 9.0$ and a number which fills the relation of $0 \leq 1-y-z \leq 0.5$, respectively, and Q shows one which is chosen from the group which consists of Mg, aluminum, calcium, Fe, and Co of metal atoms.]

[Claim 3] The manufacture approach of claim 1 whose stratified lithium nickel manganese multiple oxide fine particles after after treatment are the things of specific surface area of 0.1-10.0m² / g by the BET adsorption method, or stratified lithium nickel manganese multiple oxide fine particles given in either of 2.

[Claim 4] The manufacture approach of stratified lithium nickel manganese multiple oxide fine particles according to claim 1 to 3 that the stratified lithium nickel manganese multiple oxide fine particles after after treatment are things with a tap density of 0.8-3.0g [/cc].

[Claim 5] The manufacture approach of stratified lithium nickel manganese multiple oxide fine particles according to claim 1 to 4 that the stratified lithium nickel manganese multiple oxide fine particles after after treatment are 1.10 or more ratios [to the tap density before the after treatment of the tap density] things.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the manufacture approach of stratified lithium nickel manganese multiple oxide fine particles, especially this invention has whenever [high bulk density], and relates to the manufacture approach of suitable stratified lithium nickel manganese multiple oxide fine particles to use as positive active material of a lithium secondary battery.

[0002]

[Description of the Prior Art] Conventionally a lithium secondary battery is excellent in a high energy consistency, high power density, etc. Since-izing can be carried out [a miniaturization and lightweight], elongation rapid as a power source of pocket devices, such as a notebook sized personal computer, a cellular phone, and a handicap video camera, is shown. As positive active material of the lithium secondary battery A lithium, A multiple oxide with transition metals, such as cobalt, nickel, and manganese, for example, a lithium cobalt multiple oxide, lithium nickel complex oxide, a lithium manganese multiple oxide, etc. attracted attention from the cell property of high performance being acquired, and have resulted in utilization in part.

[0003] Furthermore, economical efficiency etc. is taken into consideration for the purpose of the stabilization as a multiple oxide, high-capacity-izing as a cell, or amelioration of the cell property in an elevated temperature. Research of various kinds of multiple oxides which permuted some of those transition-metals atoms by other metal atoms is also advanced. In it The stratified lithium nickel manganese multiple oxide expressed with $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ ($0 < x < 1$) attracts attention. For example, Solid State Ionics 311-318 (1992), J.Mater.Chem.1149-1155 (1996), To J.Power Sources 629-633 (1997) and J.Power Sources 46-53 (1998) The synthetic example of the single phase of the stratified multiple oxide of $0 \leq x \leq 0.5$ is reported, and the synthetic example of the single phase of $x = 0.5$, nickel/Mn=1 [i.e.,], is reported by 41st cell debate 2D20 (2000).

[0004] The dry process of, calcinating the source compound of a lithium, the source compound of transition metals like the above, etc. as the manufacture approach of these multiple oxides, on the other hand, for example, after grinding and mixing, or the slurry which media, such as water, were made to distribute the source compound of a lithium, the source compound of transition metals like the above, etc., and was ground and mixed -- or Although there are approaches, such as a wet method of calcinating, after drying the slurry which media, such as water, were made to distribute and was mixed after grinding the source compound of a lithium, the source compound of transition metals like the above, etc. by spray drying etc. Since the multiple oxide fine particles obtained can be formed spherically and the fine particles of whenever [high bulk density] are easy to be obtained, it considers as the approach the direction of a latter wet method is excellent.

[0005] According to this invention person's etc. examination, however, the stratified lithium

nickel manganese multiple oxide known conventionally Even if it is the multiple oxide manufactured by said wet method, as compared with a spinel mold multiple oxide etc., fine-particles bulk density is low. The sake, in order to secure energy capacity fixed when it uses for a positive electrode as positive active material -- a cell -- not enlarging -- when it did not obtain and the cell was miniaturized, it became clear that it was what is inherent in problems -- only low energy capacity is obtained.

[0006]

[Problem(s) to be Solved by the Invention] This invention is made that said problem in the stratified lithium nickel manganese multiple oxide fine particles as a conventional technique should be solved, therefore this invention has whenever [high bulk density], and it aims at offering the manufacture approach of suitable stratified lithium nickel manganese multiple oxide fine particles to use as positive active material of a lithium secondary battery.

[0007]

[Means for Solving the Problem] this invention person etc. is what reached [that said purpose can be attained by performing after treatment which applies specific stress to stratified lithium nickel manganese multiple oxide fine particles as a result of inquiring wholeheartedly that said technical problem should be solved, and] header this invention. This invention to therefore, the stratified lithium nickel manganese multiple oxide fine particles which have the mole ratio [nickel/Mn] of a nickel atom [nickel] and a manganese atom [Mn] in the range of 0.7-9.0 Let the manufacture approach of stratified lithium nickel manganese multiple oxide fine particles of performing processing which applies compression shearing stress be a summary.

[0008]

[Embodiment of the Invention] As stratified lithium nickel manganese multiple oxide fine particles with which the after treatment mentioned later is presented in this invention At least the source compound of a lithium, the source compound of nickel, and the source compound of manganese Although it may be manufactured by the dry process to calcinate after grinding and mixing It is desirable to be manufactured by the wet method which is dried by spray drying and calcinates the slurry which was ground and mixed, and which contains the source compound of a lithium, the source compound of nickel, and the source compound of manganese at least.

[0009] the distribution or the solubility to a medium [in / as the source compound of a lithium, the source compound of nickel, and a source compound of manganese, each oxide of a lithium, nickel, and manganese, a hydroxide, a carbonate, a nitrate, a sulfate, an oxalate, carboxylate, an alkylation object, a halogenide, etc. are mentioned here, and / slurring out of these], the reactivity to a multiple oxide and NO_x at the time of baking, and SO_x etc. -- it is chosen in consideration of un-generating nature etc.

[0010] As the source compound of a lithium, specifically For example, Li₂ O, LiOH, LiOH-H₂ O, and Li₂ CO₃, LiNO₃, LiOCOCH₃, Li₃ 3 (OCOC) H₄ OH (lithium citrate), LiCH₃, LiC two H₅, LiCl, LiI, etc. are mentioned. In inside LiOH-H₂ O, Li₂ CO₃, LiNO₃, and LiCH₃ CO₂ It is desirable and especially LiOH-H₂ O is desirable.

[0011] As a source compound of nickel, moreover, specifically For example, NiCO₃, 2nickel (OH)₂, and NiO, nickel (OH)₂, NiOOH, and 4H₂ O, nickel(NO₃)₂.6H₂ O, NiSO₄, NiSO₄ and 6H₂ O, and nickel(OCO) 2 and 2H₂ O nickel (OCOCH₃)₂ and NiCl₂ It is mentioned. etc. -- in inside NiCO₃, 2nickel(OH)₂ and NiO, nickel (OH)₂, NiOOH, and 4H₂ O, and NiC₂ O₄ and 2H₂ O are desirable, and NiO, nickel (OH)₂, and especially NiOOH are desirable.

[0012] As a source of manganese, specifically Moreover, for example, MnO₂ and Mn 2O₃, Mn 3O₄, MnOOH, MnCO₃, Mn (NO₃)₂, MnSO₄, Mn (OCOCH₃)₂, Mn (OCOCH₃)₃, MnCl₂, and MnCi₃ It is mentioned. etc. -- in inside MnO₂, Mn 2O₃, Mn 3O₄, and MnOOH are desirable, and they are MnO₂, Mn 2O₃, and Mn 3O₄. It is especially desirable.

[0013] In addition, in said wet method made desirable as each compound of said source of a

lithium, the source of nickel, and the source of manganese, also when it dissociates to a cation and an anion and exists as a lithium cation, a nickel cation, or a manganese cation in a slurry medium the outside in the case of existing in a slurry medium in the state of a compound, it shall contain.

[0014] Moreover, one which is chosen from the group which consists of the source compound of magnesium, the source compound of aluminum, the source compound of calcium, an iron source compound, and a source compound of cobalt besides said source compound of a lithium, the source compound of nickel, and the source compound of manganese as a source of a multiple oxide of the stratified lithium nickel manganese multiple oxide in this invention of compounds may be used further.

[0015] Here as the source compound of magnesium, the source compound of aluminum, the source compound of calcium, an iron source compound, and a source compound of cobalt Although each oxide of magnesium, aluminum, calcium, iron, and cobalt, a hydroxide, a carbonate, a nitrate, a sulfate, an oxalate, a tungstate, carboxylate, an alkylation object, halogenation, carbide, etc. are mentioned the distribution or the solubility to the medium in slurring out of these, the reactivity to a multiple oxide and NO_x at the time of baking, and SO_x etc. -- it is chosen in consideration of un-generating nature etc.

[0016] As the source compound of magnesium, specifically for example, Mg(NO₃)₂ and [MgO, Mg(OH)₂, and] 6H₂O, MgSO₄, Mg(OCO)₂ and 2H₂O, Mg(OCOCH₃)₂ and 4H₂O, and MgCl₂ It is mentioned. etc. -- in inside MgO and Mg₂(OH) It is desirable and is Mg(OH)₂. It is especially desirable.

[0017] moreover -- as the source compound of aluminum -- concrete -- for example, aluminum (NO₃)₃ and aluminum 2O₃, aluminum (OH)₃, AlOOH, and 9H₂O, Al₂(SO₄)₃, and AlCl₃ etc. -- it is mentioned, and aluminum 2O₃, aluminum (OH)₃, and AlOOH are desirable, and especially AlOOH is desirable in inside.

[0018] As a source compound of calcium, moreover, specifically For example, CaO, calcium (OH)₂, CaCO₃, calcium(NO₃)₂ and 4H₂O, CaSO₄ and 2H₂O, calcium(OCO)₂ and H₂O, CaWO₄, calcium(OCOCH₃)₂ and H₂O, CaCl₂, and CaC₂ etc. -- it mentions -- having -- inside -- CaO, calcium (OH)₂, and CaCO₃ desirable -- calcium (OH)₂ It is especially desirable.

[0019] As an iron source compound, specifically Moreover, for example, Fe₂O₃ and Fe₃O₄, Fe(NO₃)₃ and FeOOH and 9H₂O, FeSO₄ and 7H₂O, Fe₂(SO₄)₃ and nH₂O, Fe(OCO)₂ and 2H₂O, FeCl₂, and FeCl₃ It is mentioned. etc. -- in inside Fe₂O₃, Fe₃O₄, and FeOOH are desirable, and Fe₂O₃ and especially FeOOH are desirable.

[0020] As a source compound of cobalt, moreover, specifically For example, CoO, Co₂O₃, Co₃O₄, and Co(OH)₂, Co(NO₃)₂ and 6H₂O, Co(SO₄)₂·7H₂O, Co(OCOCH₃)₂ and 4H₂O, and CoCl₂ etc. -- it mentions -- having -- inside -- CoO, Co₂O₃, Co₃O₄, and Co(OH)₂ desirable -- Co(OH)₂ It is especially desirable.

[0021] In addition, in said source compound of magnesium, the source compound of aluminum, the source compound of calcium, an iron source compound, and the source compound of cobalt, the source compound of magnesium, the source compound of aluminum, and the source compound of cobalt are desirable, and the source compound of aluminum and especially the source compound of cobalt are desirable. Moreover, in said wet method made desirable also as each of these compounds, also when it dissociates to a cation and an anion and exists in a slurry medium as a magnesium cation, an aluminum cation, a calcium cation, an iron cation, or a cobalt cation the outside in the case of existing in a slurry medium in the state of a compound, it shall contain.

[0022] And the stratified lithium nickel manganese multiple oxide fine particles with which the after treatment mentioned later is presented in this invention require that the mole ratio [nickel/Mn] of a nickel atom [nickel] and a manganese atom [Mn] should be in the range of 0.7-

9.0, it is desirable that it is in the range of 0.8-1.2 as nickel/Mn, and it is [it is still more desirable that it is in the range of 0.9-1.1, and] desirable [fine particles] that it is especially in the range of 0.95-1.05. Under in said range, it becomes difficult to compound a stratified lithium nickel manganese multiple oxide with a single phase, and, on the other hand, the value of nickel/Mn becomes disadvantageous in respect of economical efficiency by said excess of the range.

[0023] Moreover, in said wet method made desirable, said source compound of a lithium, the source compound of nickel, and the source compound of manganese are contained at least. The need is accepted. Said source compound of magnesium, the source compound of aluminum, As a slurry containing one which is chosen from the group which consists of the source compound of calcium, an iron source compound, and a source compound of cobalt of compounds or [grinding and mixing by adding these compounds into media, such as water, using wet grinding mills, such as a medium stirring type grinder,] -- or After grinding these compounds using dry mills, such as a hammer mill, a roll mill, a ball mill, and a jet mill, it is prepared by the approach of mixing [be / it / under / media /, such as water, / adding], but it is desirable when a slurry with the uniform former approach pulverized and mixed in media, such as water, is obtained.

[0024] Moreover, when setting to said wet method made desirable, usually considering as 12.5 % of the weight or more preferably 10% of the weight or more when securing in the optimal range the fine-particles particle diameter formed of the spray drying mentioned later as solid content concentration with the whole compound in a slurry, and securing a uniform slurry, it may usually be 35 or less % of the weight preferably 50 or less % of the weight.

[0025] Moreover, although the mean particle diameter of each compound in a slurry is controllable by the above-mentioned grinding mixing approach and its condition When securing whenever [reactivity / in baking mentioned later /, and high bulk density] as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device Usually, it is referred to as 0.5 micrometers or less still more preferably, and 1 micrometer or less 0.05 micrometers or more 2 micrometers or less is 0.01 micrometers or more usually preferably set to 0.1 micrometers or more still more preferably from the field of economical efficiency.

[0026] Moreover, as viscosity of a slurry, as a value measured with BM mold viscometer, when securing in the optimal range the fine-particles particle diameter formed of the spray drying mentioned later Usually, when carrying out to more than 200mPa(s) and a second still more preferably and securing the handling nature of a slurry more than 100mPa(s) and a second preferably more than 50mPa(s) and a second, below 1600mPa(s) and a second take below 2000mPa(s) and a second still more preferably preferably below usual 3000mPa and a second.

[0027] Moreover, in said wet method made desirable, said slurry which was ground and mixed and which contains said source compound of a lithium, the source compound of nickel, and the source compound of manganese at least is dried by spray drying, and stratified lithium nickel manganese multiple oxide fine particles are manufactured by calcinating.

[0028] Here, spray drying is the well-known drying method for making it dry quickly and obtaining fine particles, while carrying out spraying scattering of said slurry into the gas style heated by drop-izing and conveying by this gas style, and a rotary atomizer, a two fluid nozzle mold, or a 4 hydraulic-nozzle mold spray dryer is mentioned as the equipment, for example. moreover, air, nitrogen, etc. use as a pressurization gas at the time of drop-izing -- having -- as the gas linear velocity -- usually -- it is preferably made still more desirable in 300m/second or more a second 200m /or more a second 100m /or more, and usually carries out in 1000m/second or less. Moreover, as a heated gas style, it considers as 70 degrees C or more preferably, and 50 degrees C or more 120 degrees C or less are usually preferably made into the temperature of 100 degrees C or less.

[0029] By this spray drying, the globular form fine particles as grinding mixture of each of said

compound are obtained. Although the mean particle diameter of the fine particles is controllable by the above-mentioned spraying approach, nozzle dimensions, pressurization gas jet velocity, the slurry speed of supply, heating gas style temperature, etc., as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device, it is set to 30 micrometers or less still more preferably, and is usually preferably set to 5 micrometers or more 4 micrometers or more 50 micrometers or less.

[0030] Within equipments, such as for example, a core box furnace, a tube furnace, a continuous furnace, and rotary kiln, under oxygen content gas, such as air, an oxygen gas ambient atmosphere, or inert gas ambient atmospheres, such as nitrogen and an argon, preferably, the fine particles obtained by said spray drying are heat-treated under oxygen content gas or an oxygen gas ambient atmosphere, and are calcinated.

[0031] As a burning temperature in that case, when securing reactivity, when forming the stratified multiple oxide which considers as 800 degrees C or more still more preferably, and does not have a defect, 750 degrees C or more preferably 700 degrees C or more usually. Usually, as heating time in that case, it considers as about 0.5 - 50 hours, and it is preferably desirable [after heat-treatment] in addition to cool [which is made into 950 degrees C or less still more preferably] slowly at the rate of the following by 5-degree-C/1000 degrees C or less 1050 degrees C or less.

[0032] The manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention makes it indispensable to perform after treatment which applies compression shearing stress to the stratified lithium nickel manganese multiple oxide fine particles which were manufactured by carrying out like the above.

[0033] While carrying out the load of compression and the shearing stress and compressing a fine-particles particle into a multiple oxide fine-particles particle here with the after treatment which applies compression shearing stress. The processing which makes the so-called mechano fusion accompanied by the operation to which a particle front face is made to carry out remelting arrival of the fines generated when a part of front face of a fine-particles particle is deleted by the load stress discover is said. Specifically For example, a cylinder rotating drum, The 1st arm equipped with the press shear head of the semi-sphere configuration which is fixed to the medial axis in this drum, and touches the inner skin of a drum at a tip, A predetermined include angle is separated ahead [of a rotating drum / rotation], it is fixed to a medial axis, and processing is made using the processor which consisted of the 2nd arm equipped with the pawl of the shape of an acute angle which touches the inner skin of a drum at the tip.

[0034] In this invention, "AM-15F" marketed from the HOSOKAWA chemical company, "AF-20FS", "AM-35F", "AM-60F", "AM-80F", "AM-110F", etc. are mentioned as a processor used for this processing, for example.

[0035] As for the stratified lithium nickel manganese multiple oxide in the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention, it is desirable that it is the multiple oxide expressed with the following general formula (I).

[0036]

[Formula 2]

$$\text{Li}_x \text{Ni}_y \text{Mn}_z \text{Q}_{(1-Y-Z)} \text{O}_2 \text{ (I)}$$

[0037] x are the number of $0 < x \leq 1.2$ among [type (I), y and z are $0.7 \leq y/z \leq 9.0$ and a number which fills the relation of $0 \leq 1-y-z \leq 0.5$, respectively, and Q shows one which is chosen from the group which consists of Mg, aluminum, calcium, Fe, and Co of metal atoms.]

[0038] In said formula (I), it is desirable that it is $0 < x \leq 1.1$, and x becomes unstable [the crystal structure] as a stratified multiple oxide in said excess of the range, and when it uses for a cell, it becomes the inclination which causes the fall of cell capacity. Moreover, it is desirable that it is $0.8 \leq y/z \leq 1.2$, it is still more desirable that it is $0.9 \leq y/z \leq 1.1$, and it is desirable that

it is especially $0.95 \leq y/z \leq 1.05$. It becomes a difficult inclination that y/z obtains a stratified multiple oxide with a single phase under in said range, and, on the other hand, it becomes disadvantageous in respect of economical efficiency by said excess of the range. Moreover, it is desirable that it is $0 \leq 1-y-z \leq 0.35$, and it is still more desirable that it is $0 \leq 1-y-z \leq 0.25$. In said excess of the range, when $1-y-z$ uses for a cell, it serves as an inclination which causes the fall of cell capacity.

[0039] Moreover, as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device, 0.02 micrometers or more of first [an average of] particle diameter are 0.01 micrometers or more usually 0.1 micrometers or more still more preferably preferably, and 5 micrometers or less of stratified lithium nickel manganese multiple oxide fine particles by the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention are 30 micrometers or less usually a thing 25 micrometers or less still more preferably preferably. moreover, it is 4 micrometers or more preferably, and the second [an average of] particle diameter is also that [40 micrometers or less] preferably, and usually comes out 50 micrometers or less 1 micrometers or more. Moreover, the specific surface area by the BET adsorption method is more than $4.0 \text{ m}^2 / \text{g}$ preferably, and is usually as follows [$8.0 \text{ m}^2 / \text{g}$] preferably below $10.0 \text{ m}^2 / \text{g}$ more than $0.1 \text{ m}^2 / \text{g}$.

[0040] Moreover, 0.8 g /or more of tap density after the 200 times tap as fine-particles pack density is [cc] 1.0 g/cc or more still more preferably preferably, and 3.0 g /or less of stratified lithium nickel manganese multiple oxide fine particles by the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention is [cc] a thing 2.5 g [cc] or less still more preferably preferably. And preferably, the ratio to the tap density before compression shear processing of the tap density becomes 1.15 or more still more preferably, and shows the remarkable amelioration effectiveness in bulk density 1.10 or more. In addition, although the amelioration effectiveness becomes remarkable so that this ratio is large, it is five or less ten or less especially practical.

[0041] Since the stratified lithium nickel manganese multiple oxide fine particles by the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention have whenever [high bulk density], they are suitable to use as positive active material of a lithium secondary battery.

[0042] The usage as positive active material of the lithium secondary battery of the stratified lithium nickel manganese multiple oxide fine particles obtained by the manufacture approach of this invention is conventionally based on a well-known approach. That is, after making a current collection body surface apply and dry the coating liquid which the stratified lithium nickel manganese multiple oxide fine particles of this invention as positive active material were added [coating liquid], and made the solvent distribute an electric conduction agent for them with a binder if needed, and nothing and this coating liquid, by performing consolidation processing by the 1 shaft press, a roll press, etc. preferably, a positive-active-material content layer is formed in a current collection body surface, and it considers as a positive electrode.

[0043] As a binder used, here, for example Poly vinylidene fluoride, Resin, such as polytetrafluoroethylene, polymethylmethacrylate, and polyethylene, Styrene butadiene rubber, acrylonitrile-butadiene rubber, ethylene propylene rubber, High polymers, such as rubber, such as a fluororubber, other polyvinyl acetate, and a cellulose, again as an electric conduction agent Carbonaceous particles, such as amorphous carbon, such as carbon black, such as graphites, such as a natural graphite and an artificial graphite, and acetylene black, and needle coke, are mentioned, respectively. For example, as a solvent For example, ether system solvents, such as ethylene oxide and a tetrahydrofuran, Ketone solvent, such as a methyl ethyl ketone and a cyclohexanone, methyl acetate, Aprotic polar solvents, such as amine system solvents, such as ester solvent [, such as a methyl acrylate,], diethyl triamine, N, and N-dimethylamino

propylamine, N-methyl pyrrolidone, dimethylformamide, and dimethylacetamide, etc. are mentioned.

[0044] Moreover, as a charge collector, 1-1000 micrometers of 5-500-micrometer foils are usually preferably mentioned for thickness [steel / aluminum, stainless steel, / nickel-plating], and aluminium foil is desirable as a charge collector of a positive electrode. In addition, 1-1000 micrometers of thickness of a positive-active-material content layer are usually preferably set to 10-200 micrometers.

[0045] Moreover, when the content rate of the positive active material in a positive-active-material content layer secures a cell property, such as cell capacity, when considering as 50 % of the weight or more still more preferably 30% of the weight or more preferably 10% of the weight or more and securing the mechanical strength as an electrode etc., it may usually 99.9 or less % of the weight usually be 95 or less % of the weight still more preferably 99 or less % of the weight preferably. Moreover, when the content rate of a binder secures the mechanical strength as an electrode etc., when considering as 5 % of the weight or more still more preferably 1% of the weight or more preferably 0.1% of the weight or more and securing a cell property, such as cell capacity and conductivity, it may usually 80 or less % of the weight usually be 40 or less % of the weight still more preferably 60 or less % of the weight preferably. Moreover, when the content rate of an electric conduction agent secures a cell property, such as conductivity, when considering as 1 % of the weight or more still more preferably 0.1% of the weight or more preferably 0.01% of the weight or more and securing a cell property, such as cell capacity, it may usually 50 or less % of the weight usually be 15 or less % of the weight still more preferably 30 or less % of the weight preferably.

[0046] Moreover, after a negative electrode makes a current collection body surface apply and dry the coating liquid which made the solvent distribute a negative-electrode active material with a binder, and nothing and this coating liquid, by performing consolidation processing by the 1 shaft press, a roll press, etc. preferably, it forms a negative-electrode active material content layer in a current collection body surface, and let it be a negative electrode.

[0047] As a negative-electrode active material used, here, for example A lithium, a lithium aluminium alloy, The carbide of a graphite, and a coal system and petroleum system corks, the carbide of a coal system or a petroleum system pitch, Carbide, such as needle coke, pitch coke, phenol resin, and crystalline cellulose, Carbon black, such as furnace black and acetylene black, and SnO and SnO₂, Sn_{1-x} M_x O (M is Hg, P, B, Si, germanium, or Sb, and x is 0<= x <1.) Sn₃ O₂ (OH)₂ (M -- Mg --) 2 and Sn_{3-x} M_x O₂ it is P, B, Si, germanium, Sb, or Mn, and x is 0<= x <3. LiSiO₂, SiO₂, and LiSnO₂ etc. -- it is mentioned and the same thing is mentioned [in / in a binder a solvent, etc. / formation of said positive electrode]. Moreover, as a charge collector, foils, such as copper, nickel, stainless steel, and nickel-plating steel, are mentioned, and copper foil is desirable as a charge collector of a negative electrode.

[0048] And a lithium secondary battery consists of the positive electrode which has a positive-active-material content layer in a current collection body surface, a negative electrode which has a negative-electrode active material content layer in a current collection body surface, an electrolyte layer, and a separator made to intervene between a positive electrode and a negative electrode if needed.

[0049] As an electrolyte layer, the organic electrolytic solution made to dissolve an electrolyte in a solvent or a solid polymer electrolyte, a gel electrolyte, an inorganic solid electrolyte, etc. are used here, for example, and the organic electrolytic solution is desirable in inside.

[0050] As an electrolyte in the organic electrolytic solution, for example LiCl, LiBr, LiClO₄, LiAsF₆, LiPF₆, LiBF₄, and LiB (C six H₅)₄, LiCH₃ SO₃, LiCF₃ SO₃, and LiN (SO₂ CF₃)₂, LiN (SO₂ C two F₅)₂, LiN (SO₃ CF₃)₂, and LiC (SO₂ CF₃)₃ It is mentioned. etc. -- as a solvent For example, diethylether, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, A tetrahydrofuran, 2-

methyl tetrahydrofuran, 1,4-dioxane, Ether, such as 1, 3-dioxolane, the 4-methyl -1, and 3-dioxolane, Ketones, such as 4-methyl-2-pentanone, methyl formate, methyl acetate, Ester, such as methyl propionate, dimethyl carbonate, diethyl carbonate, Methylethyl carbonate, ethylene carbonate, propylene carbonate, Carbonate, such as butylene carbonate and vinylene carbonate Halogenated hydrocarbon, such as lactone, such as gamma-butyrolactone and gamma-valerolactone, and 1,2-dichloroethane Sulfolane system compounds, such as a sulfolane and a methyl sulfolane, an acetonitrile, Nitril, such as propionitrile, butyronitrile, valeronitrile, and a benzonitrile Aprotic polar solvents, such as phosphoric ester, such as amines, such as diethylamine, ethylenediamine, and triethanolamine, trimethyl phosphate, and phosphoric-acid triethyl, N.N-dimethylformamide, N-methyl pyrrolidone, and dimethyl sulfoxide, etc. are mentioned.

[0051] Moreover, as a separator, the fine porosity film of macromolecules, such as polyolefines, such as polyethylene and polypropylene, poly vinylidene fluoride, polytetrafluoroethylene, polyester, a polyamide, polysulfone, a polyacrylonitrile, a cellulose, and cellulose acetate, is used.

[0052]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples, unless the summary is exceeded.

[0053] The lithium-hydroxide monohydrate as a source compound of example of comparison 1 lithium $[\text{LiOH} \cdot \text{H}_2\text{O}]$, The nickel hydroxide as a source compound of nickel $[\text{nickel}(\text{OH})_2]$, The manganese sesquioxide $[\text{Mn}_2\text{O}_3]$ as a source compound of manganese by the mole ratio of each atom in the stratified lithium nickel manganese multiple oxide which can finally be obtained Lithium Atom $[\text{Li}]$: Nickel atom $[\text{nickel}]$: the amount used as manganese $[\text{atom Mn}]$ =1.05:0.50:0.50 In addition to pure water, prepare the slurry of 12.5 % of the weight of solid content concentration, and while mixing using a circuit system medium stirring mold wet grinding mill (the "die no mill KD-20B mold" by the SHIMMARU enterprises company), this slurry Wet grinding was carried out for about 6 hours until the mean particle diameter of each compound in a slurry was set to 0.3 micrometers as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device. The viscosity of this slurry was 290mPa(s) and a second as a value measured with BM mold viscometer.

[0054] Subsequently, a spray dryer ("4 hydraulic-nozzle mold spray dryer" by Fujisaki Electric) is used for the obtained slurry. As opposed to the 90-degree C heating airstream which carried out the downflow in the amount of installation for 23m³/in the rectangular direction By calcinating the obtained fine-particles particle at 900 degrees C in air for 10 hours, after making it blow off from a nozzle with the linear velocity of 300m/second with pressurization air and making it dry by spray drying, by the mole ratio Lithium Atom $[\text{Li}]$: Nickel atom $[\text{nickel}]$: The stratified lithium nickel manganese multiple oxide fine particles of manganese $[\text{atom Mn}]$ =1.05:0.50:0.50 were manufactured.

[0055] The obtained stratified lithium nickel manganese multiple oxide fine particles were particles which have a **** globular form, and when the powder X diffraction was measured, it was checked that it is the stratified lithium nickel manganese multiple oxide of *****. Moreover, when the specific surface area by the BET adsorption method was measured using the full automatic fine-particles specific-surface-area measuring device (the "AMS8000 mold" by Ohkurariken), they were 6.14m² / g. Moreover, when the fine-particles pack density after putting in and carrying out the tap of about 5g of the obtained multiple oxide fine particles to a 10ml glass measuring cylinder 200 times was measured as tap density, it was 1.12g/cc.

[0056] About 300g of the stratified lithium nickel manganese multiple oxide fine particles obtained in the example 1 of example 1 comparison was extracted, and after treatment was performed by applying compression shearing stress for 10 minutes by setting the rotational

frequency of inner piece to 2000rpm using "AM-20FS" by the HOSOKAWA chemical company.

[0057] The obtained stratified lithium nickel manganese multiple oxide fine particles were particles which have a **** globular form, and when the powder X diffraction was measured, it was checked that it is the stratified lithium nickel manganese multiple oxide of *****.

[0058] Moreover, when specific surface area was measured by the same approach also in the example 1 of a comparison, they were 9.27m² / g. Moreover, when the fine-particles pack density after putting in and carrying out the tap of about 5g of the obtained multiple oxide fine particles to a 10ml glass measuring cylinder 200 times was measured as tap density, it was 1.49g/cc and the ratio to the tap density before grinding in the example 1 of a comparison was 1.33.

[0059] The stratified lithium nickel manganese multiple oxide fine particles obtained in the example 1 of the application aforementioned comparison, and the example 1, The acetylene black as an electric conduction agent, and the polytetrafluoroethylene fine particles as a binder Mix in 75 % of the weight : 20 % of the weight : 5% of the weight of the amount which becomes comparatively, and it fabricates by the thickness from which the weight with a diameter of 9mm when piercing circularly is set to about 8mg on a sheet. From this sheet, it pierced circularly and the positive electrode was produced with a diameter of 9mm by being stuck to one side of the expanded metal made from aluminum by pressure. This positive electrode is made into a trial pole, a coin cel is constructed by making a lithium metal into a counter electrode, and it is current density 0.2 mA/cm² to this. Constant-current charge, i.e., the reaction to which a lithium ion is made to emit from a positive electrode, is performed by upper limit 4.3V. Subsequently Current density 0.2 mA/cm² The initial charge capacity [Qs (C) (mAh/g)] and initial discharge capacity [Qs (D) (mAh/g)] per positive-active-material unit weight when performing the reaction occlusion of the lithium ion is carried out [reaction] to constant-current discharge, i.e., a positive electrode, by minimum 3.0V were measured. It is the initial discharge capacity [Qs (D) (mAh/g)] Current density 11 mA/cm² With the measured discharge capacity [Qa (D) (mAh/g)], it was shown in Table 1.

[0060] Moreover, those initial discharge capacity [Qs (D) (mAh/g)] and discharge capacity [Qa (D) (mAh/g)] were converted into per unit volume from said tap density, and were written together to Table 1 as initial discharge capacity [Qs' (D) (mAh/cc)] and a discharge capacity [Qa' (D) (mAh/cc)].

[0061]

[Table 1]

表 1

	比較例 1 の 複合酸化物粉体	実施例 1 の 複合酸化物粉体
正極		
初期放電容量[Qs (D)] (mAh/g)	146. 1	141. 0
初期放電容量[Qs' (D)] (mAh/cc)	163. 6	210. 1
at 電流密度0.2mA/cm ²		
放電容量[Qa (D)] (mAh/g)	91. 88	80. 15
放電容量[Qa' (D)] (mAh/cc)	102. 9	119. 4
at 電流密度11mA/cm ²		

[0062] From the result of the above example 1 of a comparison, and an example 1, the stratified lithium nickel manganese multiple oxide fine particles of the example 1 acquired by the

manufacture approach of this invention The amelioration effectiveness of the bulk density to the stratified multiple oxide of the example 1 of a comparison is large, and it is clear to have whenever [high bulk density]. Furthermore, the lithium secondary battery using the stratified lithium nickel manganese multiple oxide fine particles of the example 1 acquired by the manufacture approach of this invention as positive active material from the result of an application It is clear to have an equivalent cell property per unit weight as compared with the case where the stratified multiple oxide of the example 1 of a comparison is used as positive active material, and to have not produced degradation on the cell property by compression shear processing etc., therefore it is clear to excel in the cell property per unit volume.

[0063]

[Effect of the Invention] According to this invention, it has whenever [high bulk density] and the approach of manufacturing suitable stratified lithium nickel manganese multiple oxide fine particles using as positive active material of a lithium secondary battery can be offered.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] About the manufacture approach of stratified lithium nickel manganese multiple oxide fine particles, especially this invention has whenever [high bulk density], and relates to the manufacture approach of suitable stratified lithium nickel manganese multiple oxide fine particles to use as positive active material of a lithium secondary battery.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Conventionally a lithium secondary battery is excellent in a high energy consistency, high power density, etc. Since-izing can be carried out [a miniaturization and lightweight], elongation rapid as a power source of pocket devices, such as a notebook sized personal computer, a cellular phone, and a handicap video camera, is shown. As positive active material of the lithium secondary battery A lithium, A multiple oxide with transition metals, such as cobalt, nickel, and manganese, for example, a lithium cobalt multiple oxide, lithium nickel complex oxide, a lithium manganese multiple oxide, etc. attracted attention from the cell property of high performance being acquired, and have resulted in utilization in part.

[0003] Furthermore, economical efficiency etc. is taken into consideration for the purpose of the stabilization as a multiple oxide, high-capacity-izing as a cell, or amelioration of the cell property in an elevated temperature. Research of various kinds of multiple oxides which permuted some of those transition-metals atoms by other metal atoms is also advanced. In it The stratified lithium nickel manganese multiple oxide expressed with $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ ($0 < x < 1$) attracts attention. For example, Solid State Ionics 311-318 (1992), J.Mater.Chem.1149-1155 (1996), To J.Power Sources 629-633 (1997) and J.Power Sources 46-53 (1998) The synthetic example of the single phase of the stratified multiple oxide of $0 \leq x \leq 0.5$ is reported, and the synthetic example of the single phase of $x = 0.5$, nickel/Mn=1 [i.e.,], is reported by 41st cell debate 2D20 (2000).

[0004] The dry process of, calcinating the source compound of a lithium, the source compound of transition metals like the above, etc. as the manufacture approach of these multiple oxides, on the other hand, for example, after grinding and mixing, or the slurry which media, such as water, were made to distribute the source compound of a lithium, the source compound of transition metals like the above, etc., and was ground and mixed -- or Although there are approaches, such as a wet method of calcinating, after drying the slurry which media, such as water, were made to distribute and was mixed after grinding the source compound of a lithium, the source compound of transition metals like the above, etc. by spray drying etc. Since the multiple oxide fine particles obtained can be formed spherically and the fine particles of whenever [high bulk density] are easy to be obtained, it considers as the approach the direction of a latter wet method is excellent.

[0005] According to this invention person's etc. examination, however, the stratified lithium nickel manganese multiple oxide known conventionally Even if it is the multiple oxide manufactured by said wet method, as compared with a spinel mold multiple oxide etc., fine-particles bulk density is low. The sake, in order to secure energy capacity fixed when it uses for a positive electrode as positive active material -- a cell -- not enlarging -- when it did not obtain and the cell was miniaturized, it became clear that it was what is inherent in problems -- only low energy capacity is obtained.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, it has whenever [high bulk density] and the approach of manufacturing suitable stratified lithium nickel manganese multiple oxide fine particles using as positive active material of a lithium secondary battery can be offered.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is made that said problem in the stratified lithium nickel manganese multiple oxide fine particles as a conventional technique should be solved, therefore this invention has whenever [high bulk density], and it aims at offering the manufacture approach of suitable stratified lithium nickel manganese multiple oxide fine particles to use as positive active material of a lithium secondary battery.

[Translation done.]

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MEANS

[Means for Solving the Problem] this invention person etc. is what reached [that said purpose can be attained by performing after treatment which applies specific stress to stratified lithium nickel manganese multiple oxide fine particles as a result of inquiring wholeheartedly that said technical problem should be solved, and] header this invention. This invention to therefore, the stratified lithium nickel manganese multiple oxide fine particles which have the mole ratio [nickel/Mn] of a nickel atom [nickel] and a manganese atom [Mn] in the range of 0.7-9.0 Let the manufacture approach of stratified lithium nickel manganese multiple oxide fine particles of performing processing which applies compression shearing stress be a summary.

[0008]

[Embodiment of the Invention] As stratified lithium nickel manganese multiple oxide fine particles with which the after treatment mentioned later is presented in this invention At least the source compound of a lithium, the source compound of nickel, and the source compound of manganese Although it may be manufactured by the dry process to calcinate after grinding and mixing It is desirable to be manufactured by the wet method which is dried by spray drying and calcinates the slurry which was ground and mixed, and which contains the source compound of a lithium, the source compound of nickel, and the source compound of manganese at least.

[0009] the distribution or the solubility to a medium [in / as the source compound of a lithium, the source compound of nickel, and a source compound of manganese, each oxide of a lithium, nickel, and manganese, a hydroxide, a carbonate, a nitrate, a sulfate, an oxalate, carboxylate, an alkylation object, a halogenide, etc. are mentioned here, and / slurring out of these], the reactivity to a multiple oxide and NO_x at the time of baking, and SO_x etc. -- it is chosen in consideration of un-generating nature etc.

[0010] As the source compound of a lithium, specifically For example, Li₂ O, LiOH, LiOH-H₂ O, and Li₂ CO₃, LiNO₃, LiOCOCH₃, Li₃ 3 (OCOC) H₄ OH (lithium citrate), LiCH₃, LiC two H₅, LiCl, LiI, etc. are mentioned. In inside LiOH-H₂ O, Li₂ CO₃, LiNO₃, and LiCH₃ CO₂ It is desirable and especially LiOH-H₂ O is desirable.

[0011] As a source compound of nickel, moreover, specifically For example, NiCO₃, 2nickel (OH)₂, and NiO, nickel (OH)₂, NiOOH, and 4H₂ O, nickel(NO₃)₂.6H₂ O, NiSO₄, NiSO₄ and 6H₂ O, and nickel(OCO) 2 and 2H₂ O nickel (OCOCH₃)₂ and NiCl₂ It is mentioned. etc. -- in inside NiCO₃, 2nickel(OH)₂ and NiO, nickel (OH)₂, NiOOH, and 4H₂ O, and NiC₂ O₄ and 2H₂ O are desirable, and NiO, nickel (OH)₂, and especially NiOOH are desirable.

[0012] As a source of manganese, specifically Moreover, for example, MnO₂ and Mn 2O₃, Mn 3O₄, MnOOH, MnCO₃, Mn (NO₃)₂, MnSO₄, Mn (OCOCH₃)₂, Mn (OCOCH₃)₃, MnCl₂, and MnCi₃ It is mentioned. etc. -- in inside MnO₂, Mn 2O₃, Mn 3O₄, and MnOOH are desirable, and they are MnO₂, Mn 2O₃, and Mn 3O₄. It is especially desirable.

[0013] In addition, in said wet method made desirable as each compound of said source of a lithium, the source of nickel, and the source of manganese, also when it dissociates to a cation

and an anion and exists as a lithium cation, a nickel cation, or a manganese cation in a slurry medium the outside in the case of existing in a slurry medium in the state of a compound, it shall contain.

[0014] Moreover, one which is chosen from the group which consists of the source compound of magnesium, the source compound of aluminum, the source compound of calcium, an iron source compound, and a source compound of cobalt besides said source compound of a lithium, the source compound of nickel, and the source compound of manganese as a source of a multiple oxide of the stratified lithium nickel manganese multiple oxide in this invention of compounds may be used further.

[0015] Here as the source compound of magnesium, the source compound of aluminum, the source compound of calcium, an iron source compound, and a source compound of cobalt Although each oxide of magnesium, aluminum, calcium, iron, and cobalt, a hydroxide, a carbonate, a nitrate, a sulfate, an oxalate, a tungstate, carboxylate, an alkylation object, halogenation, carbide, etc. are mentioned the distribution or the solubility to the medium in slurring out of these, the reactivity to a multiple oxide and NO_x at the time of baking, and SO_x etc. -- it is chosen in consideration of un-generating nature etc.

[0016] As the source compound of magnesium, specifically for example, Mg(NO₃)₂ and [MgO, Mg(OH)₂, and] 6H₂O, MgSO₄, Mg(OCO)₂ and 2H₂O, Mg(OCOCH₃)₂ and 4H₂O, and MgCl₂ It is mentioned. etc. -- in inside MgO and Mg₂(OH) It is desirable and is Mg(OH)₂. It is especially desirable.

[0017] moreover -- as the source compound of aluminum -- concrete -- for example, aluminum (NO₃)₃ and aluminum 2O₃, aluminum (OH)₃, AlOOH, and 9H₂O, Al₂(SO₄)₃, and AlCl₃ etc. -- it is mentioned, and aluminum 2O₃, aluminum (OH)₃, and AlOOH are desirable, and especially AlOOH is desirable in inside.

[0018] As a source compound of calcium, moreover, specifically For example, CaO, calcium (OH)₂, CaCO₃, calcium(NO₃)₂ and 4H₂O, CaSO₄ and 2H₂O, calcium(OCO)₂ and H₂O, CaWO₄, calcium(OCOCH₃)₂ and H₂O, CaCl₂, and CaC₂ etc. -- it mentions -- having -- inside -- CaO, calcium (OH)₂, and CaCO₃ desirable -- calcium (OH)₂ It is especially desirable.

[0019] As an iron source compound, specifically Moreover, for example, Fe₂O₃ and Fe₃O₄, Fe(NO₃)₃ and FeOOH and 9H₂O, FeSO₄ and 7H₂O, Fe₂(SO₄)₃ and nH₂O, Fe(OCO)₂ and 2H₂O, FeCl₂, and FeCl₃ It is mentioned. etc. -- in inside Fe₂O₃, Fe₃O₄, and FeOOH are desirable, and Fe₂O₃ and especially FeOOH are desirable.

[0020] As a source compound of cobalt, moreover, specifically For example, CoO, Co₂O₃, Co₃O₄, and Co(OH)₂, Co(NO₃)₂ and 6H₂O, Co(SO₄)₂·7H₂O, Co(OCOCH₃)₂ and 4H₂O, and CoCl₂ etc. -- it mentions -- having -- inside -- CoO, Co₂O₃, Co₃O₄, and Co(OH)₂ desirable -- Co(OH)₂ It is especially desirable.

[0021] In addition, in said source compound of magnesium, the source compound of aluminum, the source compound of calcium, an iron source compound, and the source compound of cobalt, the source compound of magnesium, the source compound of aluminum, and the source compound of cobalt are desirable, and the source compound of aluminum and especially the source compound of cobalt are desirable. Moreover, in said wet method made desirable also as each of these compounds, also when it dissociates to a cation and an anion and exists in a slurry medium as a magnesium cation, an aluminum cation, a calcium cation, an iron cation, or a cobalt cation the outside in the case of existing in a slurry medium in the state of a compound, it shall contain.

[0022] And the stratified lithium nickel manganese multiple oxide fine particles with which the after treatment mentioned later is presented in this invention require that the mole ratio [nickel/Mn] of a nickel atom [nickel] and a manganese atom [Mn] should be in the range of 0.7-9.0, it is desirable that it is in the range of 0.8-1.2 as nickel/Mn, and it is [it is still more

desirable that it is in the range of 0.9-1.1, and] desirable [fine particles] that it is especially in the range of 0.95-1.05. Under in said range, it becomes difficult to compound a stratified lithium nickel manganese multiple oxide with a single phase, and, on the other hand, the value of nickel/Mn becomes disadvantageous in respect of economical efficiency by said excess of the range.

[0023] Moreover, in said wet method made desirable, said source compound of a lithium, the source compound of nickel, and the source compound of manganese are contained at least. The need is accepted. Said source compound of magnesium, the source compound of aluminum, As a slurry containing one which is chosen from the group which consists of the source compound of calcium, an iron source compound, and a source compound of cobalt of compounds or [grinding and mixing by adding these compounds into media, such as water, using wet grinding mills, such as a medium stirring type grinder,] -- or After grinding these compounds using dry mills, such as a hammer mill, a roll mill, a ball mill, and a jet mill, it is prepared by the approach of mixing [be / it / under / media /, such as water, / adding], but it is desirable when a slurry with the uniform former approach pulverized and mixed in media, such as water, is obtained.

[0024] Moreover, when setting to said wet method made desirable, usually considering as 12.5 % of the weight or more preferably 10% of the weight or more when securing in the optimal range the fine-particles particle diameter formed of the spray drying mentioned later as solid content concentration with the whole compound in a slurry, and securing a uniform slurry, it may usually be 35 or less % of the weight preferably 50 or less % of the weight.

[0025] Moreover, although the mean particle diameter of each compound in a slurry is controllable by the above-mentioned grinding mixing approach and its condition When securing whenever [reactivity / in baking mentioned later /, and high bulk density] as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device Usually, it is referred to as 0.5 micrometers or less still more preferably, and 1 micrometer or less 0.05 micrometers or more 2 micrometers or less is 0.01 micrometers or more usually preferably set to 0.1 micrometers or more still more preferably from the field of economical efficiency.

[0026] Moreover, as viscosity of a slurry, as a value measured with BM mold viscometer, when securing in the optimal range the fine-particles particle diameter formed of the spray drying mentioned later Usually, when carrying out to more than 200mPa(s) and a second still more preferably and securing the handling nature of a slurry more than 100mPa(s) and a second preferably more than 50mPa(s) and a second, below 1600mPa(s) and a second take below 2000mPa(s) and a second still more preferably preferably below usual 3000mPa and a second.

[0027] Moreover, in said wet method made desirable, said slurry which was ground and mixed and which contains said source compound of a lithium, the source compound of nickel, and the source compound of manganese at least is dried by spray drying, and stratified lithium nickel manganese multiple oxide fine particles are manufactured by calcinating.

[0028] Here, spray drying is the well-known drying method for making it dry quickly and obtaining fine particles, while carrying out spraying scattering of said slurry into the gas style heated by drop-izing and conveying by this gas style, and a rotary atomizer, a two fluid nozzle mold, or a 4 hydraulic-nozzle mold spray dryer is mentioned as the equipment, for example. moreover, air, nitrogen, etc. use as a pressurization gas at the time of drop-izing -- having -- as the gas linear velocity -- usually -- it is preferably made still more desirable in 300m/second or more a second 200m /or more a second 100m /or more, and usually carries out in 1000m/second or less. Moreover, as a heated gas style, it considers as 70 degrees C or more preferably, and 50 degrees C or more 120 degrees C or less are usually preferably made into the temperature of 100 degrees C or less.

[0029] By this spray drying, the globular form fine particles as grinding mixture of each of said compound are obtained. Although the mean particle diameter of the fine particles is controllable

by the above-mentioned spraying approach, nozzle dimensions, pressurization gas jet velocity, the slurry speed of supply, heating gas style temperature, etc., as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device, it is set to 30 micrometers or less still more preferably, and is usually preferably set to 5 micrometers or more 4 micrometers or more 50 micrometers or less.

[0030] Within equipments, such as for example, a core box furnace, a tube furnace, a continuous furnace, and rotary kiln, under oxygen content gas, such as air, an oxygen gas ambient atmosphere, or inert gas ambient atmospheres, such as nitrogen and an argon, preferably, the fine particles obtained by said spray drying are heat-treated under oxygen content gas or an oxygen gas ambient atmosphere, and are calcinated.

[0031] As a burning temperature in that case, when securing reactivity, when forming the stratified multiple oxide which considers as 800 degrees C or more still more preferably, and does not have a defect, 750 degrees C or more preferably 700 degrees C or more usually Usually, as heating time in that case, it considers as about 0.5 - 50 hours, and it is preferably desirable [after heat-treatment] in addition to cool [which is made into 950 degrees C or less still more preferably] slowly at the rate of the following by 5-degree-C/1000 degrees C or less 1050 degrees C or less.

[0032] The manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention makes it indispensable to perform after treatment which applies compression shearing stress to the stratified lithium nickel manganese multiple oxide fine particles which were manufactured by carrying out like the above.

[0033] While carrying out the load of compression and the shearing stress and compressing a fine-particles particle into a multiple oxide fine-particles particle here with the after treatment which applies compression shearing stress The processing which makes the so-called mechano fusion accompanied by the operation to which a particle front face is made to carry out remelting arrival of the fines generated when a part of front face of a fine-particles particle is deleted by the load stress discover is said. Specifically For example, a cylinder rotating drum, The 1st arm equipped with the press shear head of the semi-sphere configuration which is fixed to the medial axis in this drum, and touches the inner skin of a drum at a tip, A predetermined include angle is separated ahead [of a rotating drum / rotation], it is fixed to a medial axis, and processing is made using the processor which consisted of the 2nd arm equipped with the pawl of the shape of an acute angle which touches the inner skin of a drum at the tip.

[0034] In this invention, "AM-15F" marketed from the HOSOKAWA chemical company, "AF-20FS", "AM-35F", "AM-60F", "AM-80F", "AM-110F", etc. are mentioned as a processor used for this processing, for example.

[0035] As for the stratified lithium nickel manganese multiple oxide in the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention, it is desirable that it is the multiple oxide expressed with the following general formula (I).

[0036]

[Formula 2]

$Lix Niy Mnz Q(1-Y-Z) O_2$ (I)

[0037] x are the number of $0 < x \leq 1.2$ among [type (I), y and z are $0.7 \leq y/z \leq 9.0$ and a number which fills the relation of $0 \leq 1-y-z \leq 0.5$, respectively, and Q shows one which is chosen from the group which consists of Mg, aluminum, calcium, Fe, and Co of metal atoms.]

[0038] In said formula (I), it is desirable that it is $0 < x \leq 1.1$, and x becomes unstable [the crystal structure] as a stratified multiple oxide in said excess of the range, and when it uses for a cell, it becomes the inclination which causes the fall of cell capacity. Moreover, it is desirable that it is $0.8 \leq y/z \leq 1.2$, it is still more desirable that it is $0.9 \leq y/z \leq 1.1$, and it is desirable that it is especially $0.95 \leq y/z \leq 1.05$. It becomes a difficult inclination that y/z obtains a stratified

multiple oxide with a single phase under in said range, and, on the other hand, it becomes disadvantageous in respect of economical efficiency by said excess of the range. Moreover, it is desirable that it is $0 \leq 1-y-z \leq 0.35$, and it is still more desirable that it is $0 \leq 1-y-z \leq 0.25$. In said excess of the range, when 1-y-z uses for a cell, it serves as an inclination which causes the fall of cell capacity.

[0039] Moreover, as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device, 0.02 micrometers or more of first [an average of] particle diameter are 0.01 micrometers or more usually 0.1 micrometers or more still more preferably preferably, and 5 micrometers or less of stratified lithium nickel manganese multiple oxide fine particles by the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention are 30 micrometers or less usually a thing 25 micrometers or less still more preferably preferably. moreover, it is 4 micrometers or more preferably, and the second [an average of] particle diameter is also that [40 micrometers or less] preferably, and usually comes out 50 micrometers or less 1 micrometers or more. Moreover, the specific surface area by the BET adsorption method is more than $4.0 \text{ m}^2 / \text{g}$ preferably, and is usually as follows [$8.0 \text{ m}^2 / \text{g}$] preferably below $10.0 \text{ m}^2 / \text{g}$ more than $0.1 \text{ m}^2 / \text{g}$.

[0040] Moreover, 0.8g /or more of tap density after the 200 times tap as fine-particles pack density is [cc] 1.0 g/cc or more still more preferably preferably, and 3.0g /or less of stratified lithium nickel manganese multiple oxide fine particles by the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention is [cc] a thing 2.5 g/cc or less still more preferably preferably. And preferably, the ratio to the tap density before compression shear processing of the tap density becomes 1.15 or more still more preferably, and shows the remarkable amelioration effectiveness in bulk density 1.10 or more. In addition, although the amelioration effectiveness becomes remarkable so that this ratio is large, it is five or less ten or less especially practical.

[0041] Since the stratified lithium nickel manganese multiple oxide fine particles by the manufacture approach of the stratified lithium nickel manganese multiple oxide fine particles of this invention have whenever [high bulk density], they are suitable to use as positive active material of a lithium secondary battery.

[0042] The usage as positive active material of the lithium secondary battery of the stratified lithium nickel manganese multiple oxide fine particles obtained by the manufacture approach of this invention is conventionally based on a well-known approach. That is, after making a current collection body surface apply and dry the coating liquid which the stratified lithium nickel manganese multiple oxide fine particles of this invention as positive active material were added [coating liquid], and made the solvent distribute an electric conduction agent for them with a binder if needed, and nothing and this coating liquid, by performing consolidation processing by the 1 shaft press, a roll press, etc. preferably, a positive-active-material content layer is formed in a current collection body surface, and it considers as a positive electrode.

[0043] As a binder used, here, for example Poly vinylidene fluoride, Resin, such as polytetrafluoroethylene, polymethylmethacrylate, and polyethylene, Styrene butadiene rubber, acrylonitrile-butadiene rubber, ethylene propylene rubber, High polymers, such as rubber, such as a fluororubber, other polyvinyl acetate, and a cellulose, again as an electric conduction agent Carbonaceous particles, such as amorphous carbon, such as carbon black, such as graphites, such as a natural graphite and an artificial graphite, and acetylene black, and needle coke, are mentioned, respectively. For example, as a solvent For example, ether system solvents, such as ethylene oxide and a tetrahydrofuran, Ketone solvent, such as a methyl ethyl ketone and a cyclohexanone, methyl acetate, Aprotic polar solvents, such as amine system solvents, such as ester solvent [, such as a methyl acrylate,], diethyl triamine, N, and N-dimethylamino propylamine, N-methyl pyrrolidone, dimethylformamide, and dimethylacetamide, etc. are

mentioned.

[0044] Moreover, as a charge collector, 1-1000 micrometers of 5-500-micrometer foils are usually preferably mentioned for thickness [steel / aluminum, stainless steel, / nickel-plating], and aluminium foil is desirable as a charge collector of a positive electrode. In addition, 1-1000 micrometers of thickness of a positive-active-material content layer are usually preferably set to 10-200 micrometers.

[0045] Moreover, when the content rate of the positive active material in a positive-active-material content layer secures a cell property, such as cell capacity, when considering as 50 % of the weight or more still more preferably 30% of the weight or more preferably 10% of the weight or more and securing the mechanical strength as an electrode etc., it may usually 99.9 or less % of the weight usually be 95 or less % of the weight still more preferably 99 or less % of the weight preferably. Moreover, when the content rate of a binder secures the mechanical strength as an electrode etc., when considering as 5 % of the weight or more still more preferably 1% of the weight or more preferably 0.1% of the weight or more and securing a cell property, such as cell capacity and conductivity, it may usually 80 or less % of the weight usually be 40 or less % of the weight still more preferably 60 or less % of the weight preferably. Moreover, when the content rate of an electric conduction agent secures a cell property, such as conductivity, when considering as 1 % of the weight or more still more preferably 0.1% of the weight or more preferably 0.01% of the weight or more and securing a cell property, such as cell capacity, it may usually 50 or less % of the weight usually be 15 or less % of the weight still more preferably 30 or less % of the weight preferably.

[0046] Moreover, after a negative electrode makes a current collection body surface apply and dry the coating liquid which made the solvent distribute a negative-electrode active material with a binder, and nothing and this coating liquid, by performing consolidation processing by the 1 shaft press, a roll press, etc. preferably, it forms a negative-electrode active material content layer in a current collection body surface, and let it be a negative electrode.

[0047] As a negative-electrode active material used, here, for example A lithium, a lithium aluminium alloy, The carbide of a graphite, and a coal system and petroleum system corks, the carbide of a coal system or a petroleum system pitch, Carbide, such as needle coke, pitch coke, phenol resin, and crystalline cellulose, Carbon black, such as furnace black and acetylene black, and SnO and SnO₂, Sn_{1-x} M_x O (M is Hg, P, B, Si, germanium, or Sb, and x is 0≤x<1.) Sn₃ O₂ (OH)₂ (M -- Mg --) 2 and Sn_{3-x} M_x O₂ it is P, B, Si, germanium, Sb, or Mn, and x is 0≤x<3. LiSiO₂, SiO₂, and LiSnO₂ etc. -- it is mentioned and the same thing is mentioned [in / in a binder a solvent, etc. / formation of said positive electrode]. Moreover, as a charge collector, foils, such as copper, nickel, stainless steel, and nickel-plating steel, are mentioned, and copper foil is desirable as a charge collector of a negative electrode.

[0048] And a lithium secondary battery consists of the positive electrode which has a positive-active-material content layer in a current collection body surface, a negative electrode which has a negative-electrode active material content layer in a current collection body surface, an electrolyte layer, and a separator made to intervene between a positive electrode and a negative electrode if needed.

[0049] As an electrolyte layer, the organic electrolytic solution made to dissolve an electrolyte in a solvent or a solid polymer electrolyte, a gel electrolyte, an inorganic solid electrolyte, etc. are used here, for example, and the organic electrolytic solution is desirable in inside.

[0050] As an electrolyte in the organic electrolytic solution, for example LiCl, LiBr, LiClO₄, LiAsF₆, LiPF₆, LiBF₄, and LiB (C six H₅)₄, LiCH₃ SO₃, LiCF₃ SO₃, and LiN (SO₂ CF₃)₂, LiN (SO₂ C two F₅)₂, LiN (SO₃ CF₃)₂, and LiC (SO₂ CF₃)₃ It is mentioned. etc. -- as a solvent For example, diethylether, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, A tetrahydrofuran, 2-methyl tetrahydrofuran, 1,4-dioxane, Ether, such as 1, 3-dioxolane, the 4-methyl -1, and 3-

dioxolane, Ketones, such as 4-methyl-2-pentanone, methyl formate, methyl acetate, Ester, such as methyl propionate, dimethyl carbonate, diethyl carbonate, Methylethyl carbonate, ethylene carbonate, propylene carbonate, Carbonate, such as butylene carbonate and vinylene carbonate Halogenated hydrocarbon, such as lactone, such as gamma-butyrolactone and gamma-valerolactone, and 1,2-dichloroethane Sulfolane system compounds, such as a sulfolane and a methyl sulfolane, an acetonitrile, Nitril, such as propionitrile, butyronitrile, valeronitrile, and a benzonitrile Aprotic polar solvents, such as phosphoric ester, such as amines, such as diethylamine, ethylenediamine, and triethanolamine, trimethyl phosphate, and phosphoric-acid triethyl, N.N-dimethylformamide, N-methyl pyrrolidone, and dimethyl sulfoxide, etc. are mentioned.

[0051] Moreover, as a separator, the fine porosity film of macromolecules, such as polyolefines, such as polyethylene and polypropylene, poly vinylidene fluoride, polytetrafluoroethylene, polyester, a polyamide, polysulfone, a polyacrylonitrile, a cellulose, and cellulose acetate, is used.

[Translation done.]

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EXAMPLE

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples, unless the summary is exceeded.

[0053] The lithium-hydroxide monohydrate as a source compound of example of comparison 1 lithium [LiOH-H₂O], The nickel hydroxide as a source compound of nickel [nickel (OH)₂], The manganese sesquioxide [Mn₂O₃] as a source compound of manganese by the mole ratio of each atom in the stratified lithium nickel manganese multiple oxide which can finally be obtained Lithium Atom,[Li]: Nickel atom [nickel] : the amount used as manganese [atom Mn] =1.05:0.50:0.50 In addition to pure water, prepare the slurry of 12.5 % of the weight of solid content concentration, and while mixing using a circuit system medium stirring mold wet grinding mill (the "die no mill KD-20B mold" by the SHIMMARU enterprises company), this slurry Wet grinding was carried out for about 6 hours until the mean particle diameter of each compound in a slurry was set to 0.3 micrometers as a value measured with laser diffraction / dispersion type particle-size-distribution measuring device. The viscosity of this slurry was 290mPa(s) and a second as a value measured with BM mold viscometer.

[0054] Subsequently, a spray dryer ("4 hydraulic-nozzle mold spray dryer" by Fujisaki Electric) is used for the obtained slurry. As opposed to the 90-degree C heating airstream which carried out the downflow in the amount of installation for 23m³/in the rectangular direction By calcinating the obtained fine-particles particle at 900 degrees C in air for 10 hours, after making it blow off from a nozzle with the linear velocity of 300m/second with pressurization air and making it dry by spray drying, by the mole ratio Lithium Atom [Li]: Nickel atom [nickel]: The stratified lithium nickel manganese multiple oxide fine particles of manganese [atom Mn] =1.05:0.50:0.50 were manufactured.

[0055] The obtained stratified lithium nickel manganese multiple oxide fine particles were particles which have a **** globular form, and when the powder X diffraction was measured, it was checked that it is the stratified lithium nickel manganese multiple oxide of *****. Moreover, when the specific surface area by the BET adsorption method was measured using the full automatic fine-particles specific-surface-area measuring device (the "AMS8000 mold" by Ohkurariken), they were 6.14m² / g. Moreover, when the fine-particles pack density after putting in and carrying out the tap of about 5g of the obtained multiple oxide fine particles to a 10ml glass measuring cylinder 200 times was measured as tap density, it was 1.12g/cc.

[0056] About 300g of the stratified lithium nickel manganese multiple oxide fine particles obtained in the example 1 of example 1 comparison was extracted, and after treatment was performed by applying compression shearing stress for 10 minutes by setting the rotational frequency of inner piece to 2000rpm using "AM-20FS" by the HOSOKAWA chemical company.

[0057] The obtained stratified lithium nickel manganese multiple oxide fine particles were particles which have a **** globular form, and when the powder X diffraction was measured, it

was checked that it is the stratified lithium nickel manganese multiple oxide of *****.
 [0058] Moreover, when specific surface area was measured by the same approach also in the example 1 of a comparison, they were 9.27m² / g. Moreover, when the fine-particles pack density after putting in and carrying out the tap of about 5g of the obtained multiple oxide fine particles to a 10ml glass measuring cylinder 200 times was measured as tap density, it was 1.49g/cc and the ratio to the tap density before grinding in the example 1 of a comparison was 1.33.

[0059] The stratified lithium nickel manganese multiple oxide fine particles obtained in the example 1 of the application aforementioned comparison, and the example 1, The acetylene black as an electric conduction agent, and the polytetrafluoroethylene fine particles as a binder Mix in 75 % of the weight : 20 % of the weight : 5% of the weight of the amount which becomes comparatively, and it fabricates by the thickness from which the weight with a diameter of 9mm when piercing circularly is set to about 8mg on a sheet. From this sheet, it pierced circularly and the positive electrode was produced with a diameter of 9mm by being stuck to one side of the expanded metal made from aluminum by pressure. This positive electrode is made into a trial pole, a coin cel is constructed by making a lithium metal into a counter electrode, and it is current density 0.2 mA/cm² to this. Constant-current charge, i.e., the reaction to which a lithium ion is made to emit from a positive electrode, is performed by upper limit 4.3V. Subsequently Current density 0.2 mA/cm² The initial charge capacity [Qs (C) (mAh/g)] and initial discharge capacity [Qs (D) (mAh/g)] per positive-active-material unit weight when performing the reaction occlusion of the lithium ion is carried out [reaction] to constant-current discharge, i.e., a positive electrode, by minimum 3.0V were measured. It is the initial discharge capacity [Qs (D) (mAh/g)] Current density 11 mA/cm² With the measured discharge capacity [Qa (D) (mAh/g)], it was shown in Table 1.

[0060] Moreover, those initial discharge capacity [Qs (D) (mAh/g)] and discharge capacity [Qa (D) (mAh/g)] were converted into per unit volume from said tap density, and were written together to Table 1 as initial discharge capacity [Qs' (D) (mAh/cc)] and a discharge capacity [Qa' (D) (mAh/cc)].

[0061]

[Table 1]

表 1

		比較例 1 の 複合酸化物粉体	実施例 1 の 複合酸化物粉体
正極			
初期放電容量[Qs (D)]	(mAh/g)	146. 1	141. 0
初期放電容量[Qs' (D)]	(mAh/cc)	163. 6	210. 1
at 電流密度0.2mA/cm ²			
放電容量[Qa (D)]	(mAh/g)	91. 88	80. 15
放電容量[Qa' (D)]	(mAh/cc)	102. 9	119. 4
at 電流密度11mA/cm ²			

[0062] From the result of the above example 1 of a comparison, and an example 1, the stratified lithium nickel manganese multiple oxide fine particles of the example 1 acquired by the manufacture approach of this invention The amelioration effectiveness of the bulk density to the stratified multiple oxide of the example 1 of a comparison is large, and it is clear to have whenever [high bulk density]. Furthermore, the lithium secondary battery using the stratified lithium nickel manganese multiple oxide fine particles of the example 1 acquired by the

manufacture approach of this invention as positive active material from the result of an application It is clear to have an equivalent cell property per unit weight as compared with the case where the stratified multiple oxide of the example 1 of a comparison is used as positive active material, and to have not produced degradation on the cell property by compression shear processing etc., therefore it is clear to excel in the cell property per unit volume.

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(54) 【発明の名称】 層状リチウムニッケルマンガン複合酸化物粉体の製造方法

(57) 【要約】

【目的】 高嵩密度を有し、リチウム二次電池の正極活物質として用いるに好適な層状リチウムニッケルマンガン複合酸化物粉体の製造方法を提供する。

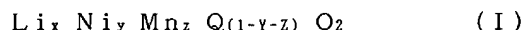
【構成】 ニッケル原子〔Ni〕とマンガン原子〔Mn〕とのモル比〔Ni/Mn〕が0.7~9.0の範囲にある層状リチウムニッケルマンガン複合酸化物粉体に、圧縮剪断応力を加える処理を施す層状リチウムニッケルマンガン複合酸化物粉体の製造方法。

【特許請求の範囲】

【請求項1】 ニッケル原子〔Ni〕とマンガン原子〔Mn〕とのモル比〔Ni/Mn〕が0.7～9.0の範囲にある層状リチウムニッケルマンガン複合酸化物粉体に、圧縮剪断応力を加える後処理を施すことを特徴とする層状リチウムニッケルマンガン複合酸化物粉体の製造方法。

【請求項2】 層状リチウムニッケルマンガン複合酸化物粉体が、下記一般式（I）で表される複合酸化物である請求項1に記載の層状リチウムニッケルマンガン複合酸化物粉体の製造方法。

【化1】



〔式（I）中、 x は、 $0 < x \leq 1$ 、2の数であり、 y 及び z はそれぞれ、 $0.7 \leq y/z \leq 9.0$ 、及び、 $0 \leq 1-y-z \leq 0.5$ の関係を満たす数であり、 Q は、Mg、Al、Ca、Fe、及びCoからなる群から選択されるいずれかの金属原子を示す。〕

【請求項3】 後処理後の層状リチウムニッケルマンガン複合酸化物粉体が、BET法による比表面積0.1～10.0 m^2/g のものである請求項1又は2のいずれかに記載の層状リチウムニッケルマンガン複合酸化物粉体の製造方法。

【請求項4】 後処理後の層状リチウムニッケルマンガン複合酸化物粉体が、タップ密度0.8～3.0 g/cc のものである請求項1乃至3のいずれかに記載の層状リチウムニッケルマンガン複合酸化物粉体の製造方法。

【請求項5】 後処理後の層状リチウムニッケルマンガン複合酸化物粉体が、そのタップ密度の後処理前のタップ密度に対する比1.10以上のものである請求項1乃至4のいずれかに記載の層状リチウムニッケルマンガン複合酸化物粉体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、層状リチウムニッケルマンガン複合酸化物粉体の製造方法に関し、特に高嵩密度を有し、リチウム二次電池の正極活物質として用いるに好適な層状リチウムニッケルマンガン複合酸化物粉体の製造方法に関する。

【0002】

【従来の技術】従来より、リチウム二次電池は、高エネルギー密度及び高出力密度等に優れ、小型化・軽量化できることから、ノート型パソコン、携帯電話、ハンディビデオカメラ等の携帯機器の電源として急激な伸びを示しており、そのリチウム二次電池の正極活物質としては、リチウムと、コバルト、ニッケル、マンガン等の遷移金属との複合酸化物、例えば、リチウムコバルト複合酸化物、リチウムニッケル複合酸化物、リチウムマンガン複合酸化物等が、高性能の電池特性が得られることから注目され、一部実用化に到っている。

【0003】更に、複合酸化物としての安定化や、電池としての高容量化或いは高温での電池特性の改良等を目的とし、経済性等も勘案して、それらの遷移金属原子の一部を他の金属原子で置換した各種の複合酸化物の研究も進められており、その中で、 $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ ($0 < x < 1$)で表される層状リチウムニッケルマンガン複合酸化物が注目され、例えば、Solid State Ionics 311-318(1992)、J. Mater. Chem. 1149-1155(1996)、J. Power Sources 629-633(1997)、J. Power Sources 46-53(1998)等には、 $0 \leq x \leq 0.5$ の層状複合酸化物の単一相の合成例が報告され、又、第41回電池討論会2020(2000)では、 $x=0.5$ 、即ちNi/Mn=1の単一相の合成例が報告されている。

【0004】一方、これらの複合酸化物の製造方法としては、例えば、リチウム源化合物と前記の如き遷移金属源化合物等を、粉碎及び混合した後、焼成する等の乾式法、又は、リチウム源化合物と前記の如き遷移金属源化合物等とを水等の媒体に分散させ粉碎及び混合したスラリーを、或いは、リチウム源化合物と前記の如き遷移金属源化合物等を粉碎した後、水等の媒体に分散させ混合したスラリーを、噴霧乾燥等により乾燥させた後、焼成する等の湿式法等の方法があるが、得られる複合酸化物粉体を球状に形成でき、高嵩密度の粉体が得られ易いことから、後者湿式法の方が優れる方法とされている。

【0005】しかしながら、本発明者等の検討によると、従来知られている層状リチウムニッケルマンガン複合酸化物は、前記湿式法によって製造される複合酸化物であっても、スピネル型複合酸化物等に比して、粉体嵩密度が低く、そのため、正極活物質として正極に用いたときに、一定のエネルギー容量を確保するためには電池を大型化せざるを得ず、又、電池を小型化すると低エネルギー容量しか得られない等の問題を内在するものであることが判明した。

【0006】

【発明が解決しようとする課題】本発明は、従来技術としての層状リチウムニッケルマンガン複合酸化物粉体における前記問題を解決すべくなされたものであって、従って、本発明は、高嵩密度を有し、リチウム二次電池の正極活物質として用いるに好適な層状リチウムニッケルマンガン複合酸化物粉体の製造方法を提供することを目的とする。

【0007】

【課題を解決するための手段】本発明者等は、前記課題を解決すべく鋭意検討した結果、層状リチウムニッケルマンガン複合酸化物粉体に特定応力を加える後処理を施すことによって前記目的を達成できることを見出し本発明に到達したもので、従って、本発明は、ニッケル原子〔Ni〕とマンガン原子〔Mn〕とのモル比〔Ni/Mn〕が0.7～9.0の範囲にある層状リチウムニッケルマンガン複合酸化物粉体に、圧縮剪断応力を加える処

理を施す層状リチウムニッケルマンガン複合酸化物粉体の製造方法、を要旨とする。

【0008】

【発明の実施の形態】本発明において、後述する後処理に供する層状リチウムニッケルマンガン複合酸化物粉体としては、少なくともリチウム源化合物とニッケル源化合物とマンガン源化合物とを、粉碎及び混合した後、焼成する乾式法により製造されたものであってもよいが、粉碎及び混合された少なくともリチウム源化合物とニッケル源化合物とマンガン源化合物とを含有するスラリーを、噴霧乾燥により乾燥させ、焼成する湿式法により製造されたものであるのが好ましい。

【0009】ここで、リチウム源化合物、ニッケル源化合物、及びマンガン源化合物としては、リチウム、ニッケル、及びマンガンの各酸化物、水酸化物、炭酸塩、硝酸塩、硫酸塩、砒酸塩、カルボン酸塩、アルキル化物、ハロゲン化物等が挙げられ、これらの中から、スラリー化における媒体への分散或いは溶解性、複合酸化物への反応性、及び、焼成時における NO_x 、 SO_x 等の非発生性等を考慮して選択される。

【0010】そのリチウム源化合物としては、具体的には、例えば、 Li_2O 、 LiOH 、 $\text{LiOH} \cdot \text{H}_2\text{O}$ 、 Li_2CO_3 、 LiNO_3 、 LiOCOCH_3 、 $\text{Li}_3(\text{OCOC})_3$ 、 H_4OH （クエン酸リチウム）、 LiCH_3 、 LiC_2H_5 、 LiCl 、 LiI 等が挙げられ、中で、 $\text{LiOH} \cdot \text{H}_2\text{O}$ 、 Li_2CO_3 、 LiNO_3 、 LiCH_3CO_2 が好ましく、 $\text{LiOH} \cdot \text{H}_2\text{O}$ が特に好ましい。

【0011】又、ニッケル源化合物としては、具体的には、例えば、 NiO 、 $\text{Ni}(\text{OH})_2$ 、 NiOOH 、 $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ 、 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 NiSO_4 、 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 、 $\text{Ni}(\text{OCO})_2 \cdot 2\text{H}_2\text{O}$ 、 $\text{Ni}(\text{OCOCH}_3)_2$ 、 NiCl_2 等が挙げられ、中で、 NiO 、 $\text{Ni}(\text{OH})_2$ 、 NiOOH 、 $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ 、 $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ が好ましく、 NiO 、 $\text{Ni}(\text{OH})_2$ 、 NiOOH が特に好ましい。

【0012】又、マンガン源としては、具体的には、例えば、 MnO_2 、 Mn_2O_3 、 Mn_3O_4 、 MnOOH 、 MnCO_3 、 $\text{Mn}(\text{NO}_3)_2$ 、 MnSO_4 、 $\text{Mn}(\text{OCOCH}_3)_2$ 、 $\text{Mn}(\text{OCOCH}_3)_3$ 、 MnCl_2 、 MnCl_3 等が挙げられ、中で、 MnO_2 、 Mn_2O_3 、 Mn_3O_4 、 MnOOH が好ましく、 MnO_2 、 Mn_2O_3 、 Mn_3O_4 が特に好ましい。

【0013】尚、前記リチウム源、ニッケル源、及びマンガン源の各化合物としては、好ましいとする前記湿式法において、化合物の状態でスラリー媒体中に存在する場合の外、スラリー媒体中でカチオンとアニオンとに解離し、リチウムカチオン、ニッケルカチオン、或いはマンガンカチオンとして存在する場合も含むものとする。

【0014】又、本発明における層状リチウムニッケルマンガン複合酸化物の複合酸化物源としては、前記リチウム源化合物、ニッケル源化合物、及びマンガン源化合物の他に、マグネシウム源化合物、アルミニウム源化合物、カルシウム源化合物、鉄源化合物、及びコバルト源化合物からなる群から選択されるいずれかの化合物が更に用いられていてもよい。

【0015】ここで、マグネシウム源化合物、アルミニウム源化合物、カルシウム源化合物、鉄源化合物、及びコバルト源化合物としては、マグネシウム、アルミニウム、カルシウム、鉄、及びコバルトの各酸化物、水酸化物、炭酸塩、硝酸塩、硫酸塩、砒酸塩、タングステン酸塩、カルボン酸塩、アルキル化物、ハロゲン化、炭化物等が挙げられるが、これらの中から、スラリー化における媒体への分散或いは溶解性、複合酸化物への反応性、及び、焼成時における NO_x 、 SO_x 等の非発生性等を考慮して選択される。

【0016】そのマグネシウム源化合物としては、具体的には、例えば、 MgO 、 $\text{Mg}(\text{OH})_2$ 、 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 MgSO_4 、 $\text{Mg}(\text{OCO})_2 \cdot 2\text{H}_2\text{O}$ 、 $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ 、 MgCl_2 等が挙げられ、中で、 MgO 、 $\text{Mg}(\text{OH})_2$ が好ましく、 $\text{Mg}(\text{OH})_2$ が特に好ましい。

【0017】又、アルミニウム源化合物としては、具体的には、例えば、 Al_2O_3 、 $\text{Al}(\text{OH})_3$ 、 AlOOH 、 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 、 $\text{Al}_2(\text{SO}_4)_3$ 、 AlCl_3 等が挙げられ、中で、 Al_2O_3 、 $\text{Al}(\text{OH})_3$ 、 AlOOH が好ましく、 AlOOH が特に好ましい。

【0018】又、カルシウム源化合物としては、具体的には、例えば、 CaO 、 $\text{Ca}(\text{OH})_2$ 、 CaCO_3 、 $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 、 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ 、 $\text{Ca}(\text{OCO})_2 \cdot \text{H}_2\text{O}$ 、 CaWO_4 、 $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ 、 CaCl_2 、 CaC_2 等が挙げられ、中で、 CaO 、 $\text{Ca}(\text{OH})_2$ 、 CaCO_3 が好ましく、 $\text{Ca}(\text{OH})_2$ が特に好ましい。

【0019】又、鉄源化合物としては、具体的には、例えば、 Fe_2O_3 、 Fe_3O_4 、 FeOOH 、 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 、 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 、 $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ 、 $\text{Fe}(\text{OCO})_2 \cdot 2\text{H}_2\text{O}$ 、 FeCl_2 、 FeCl_3 等が挙げられ、中で、 Fe_2O_3 、 Fe_3O_4 、 FeOOH が好ましく、 Fe_2O_3 、 FeOOH が特に好ましい。

【0020】又、コバルト源化合物としては、具体的には、例えば、 CoO 、 Co_2O_3 、 Co_3O_4 、 $\text{Co}(\text{OH})_2$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ 、 $\text{Co}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ 、 CoCl_2 等が挙げられ、中で、 CoO 、 Co_2O_3 、 Co_3O_4 、 $\text{Co}(\text{OH})_2$ が好ましく、 $\text{Co}(\text{OH})_2$ が特に好ましい。

【0021】尚、前記マグネシウム源化合物、アルミニウム源化合物、カルシウム源化合物、鉄源化合物、及びコバルト源化合物の中で、マグネシウム源化合物、アルミニウム源化合物、コバルト源化合物が好ましく、アルミニウム源化合物、コバルト源化合物が特に好ましい。又、これらの各化合物としても、好ましいとする前記湿式法において、化合物の状態でスラリー媒体中に存在する場合の外、スラリー媒体中でカチオンとアニオンとに解離し、マグネシウムカチオン、アルミニウムカチオン、カルシウムカチオン、鉄カチオン、或いはコバルトカチオンとして存在する場合も含むものとする。

【0022】そして、本発明においては、後述する後処理に供する層状リチウムニッケルマンガン複合酸化物粉体は、ニッケル原子〔Ni〕とマンガン原子〔Mn〕とのモル比〔Ni/Mn〕が0.7～9.0の範囲にあることが必要であり、Ni/Mnとして0.8～1.2の範囲にあるのが好ましく、0.9～1.1の範囲にあるのが更に好ましく、0.95～1.05の範囲にあるのが特に好ましい。Ni/Mnの値が前記範囲未満では、層状リチウムニッケルマンガン複合酸化物を単一相で合成することが困難となり、一方、前記範囲超過では、経済性の面で不利となる。

【0023】又、好ましいとする前記湿式法において、少なくとも前記リチウム源化合物とニッケル源化合物とマンガン源化合物とを含有し、必要に応じて、前記マグネシウム源化合物、アルミニウム源化合物、カルシウム源化合物、鉄源化合物、及びコバルト源化合物からなる群から選択されるいずれかの化合物を含有するスラリーとしては、水等の媒体中にこれらの化合物を加え、媒体攪拌式粉碎機等の湿式粉碎機を用いて粉碎及び混合するか、或いは、これらの化合物をハンマーミル、ローミル、ボールミル、ジェットミル等の乾式粉碎機を用いて粉碎した後、水等の媒体中に加え混合する等の方法により調製されるが、水等の媒体中で粉碎及び混合する前者方法が、均一なスラリーが得られる上で好ましい。

【0024】又、好ましいとする前記湿式法において、スラリー中における化合物全体による固形分濃度としては、後述する噴霧乾燥により形成される粉体粒子径を最適な範囲に確保する上で、通常10重量%以上、好ましくは12.5重量%以上とし、又、均一なスラリーを確保する上で、通常50重量%以下、好ましくは35重量%以下とする。

【0025】又、スラリー中における各化合物の平均粒子径は、前述の粉碎混合方法及びその条件により制御することができるが、レーザー回折/散乱式粒度分布測定装置により測定した値として、後述する焼成における反応性、及び高嵩密度を確保する上で、通常2 μ m以下、好ましくは1 μ m以下、更に好ましくは0.5 μ m以下とし、又、経済性の面から、通常0.01 μ m以上、好ましくは0.05 μ m以上、更に好ましくは0.1 μ m

以上とする。

【0026】又、スラリーの粘度としては、BM型粘度計により測定した値として、後述する噴霧乾燥により形成される粉体粒子径を最適な範囲に確保する上で、通常50mPa・秒以上、好ましくは100mPa・秒以上、更に好ましくは200mPa・秒以上とし、又、スラリーの取扱性を確保する上で、通常3000mPa・秒以下、好ましくは2000mPa・秒以下、更に好ましくは1600mPa・秒以下とする。

【0027】又、好ましいとする前記湿式法においては、粉碎及び混合された少なくとも前記リチウム源化合物とニッケル源化合物とマンガン源化合物とを含有する前記スラリーを、噴霧乾燥により乾燥させ、焼成することにより層状リチウムニッケルマンガン複合酸化物粉体が製造される。

【0028】ここで、噴霧乾燥とは、前記スラリーを液滴化して加熱された気体流中へ噴霧飛散させ、該気体流で搬送しながら急速に乾燥させて粉体を得る公知の乾燥法であり、その装置としては、例えば、ロータリーアトマイザー、二流体ノズル型或いは四流体ノズル型スプレードライヤー等が挙げられる。又、液滴化する際の加圧気体としては、空気、窒素等が用いられ、そのガス線速としては、通常100m/秒以上、好ましくは200m/秒以上、更に好ましくは300m/秒以上とし、通常1000m/秒以下とする。又、加熱された気体流としては、通常50℃以上、好ましくは70℃以上とし、通常120℃以下、好ましくは100℃以下の温度とする。

【0029】この噴霧乾燥により、前記各化合物の粉碎混合物としての球形状の粉体が得られる。その粉体の平均粒子径は、前述の噴霧方法、ノズル形状、加圧気体噴射速度、スラリー供給速度、加熱気体流温度等によって制御することができるが、レーザー回折/散乱式粒度分布測定装置により測定した値として、好ましくは50 μ m以下、更に好ましくは30 μ m以下とし、通常4 μ m以上、好ましくは5 μ m以上とする。

【0030】前記噴霧乾燥により得られた粉体は、例えば、箱型炉、管状炉、トンネル炉、ロータリーキルン等の装置内で、空気等の酸素含有ガス或いは酸素ガス雰囲気下、又は、窒素、アルゴン等の不活性ガス雰囲気下、好ましくは酸素含有ガス或いは酸素ガス雰囲気下、加熱処理し焼成される。

【0031】その際の焼成温度としては、反応性を確保する上で、通常700℃以上、好ましくは750℃以上、更に好ましくは800℃以上とし、又、欠陥のない層状複合酸化物を形成する上で、通常1050℃以下、好ましくは1000℃以下、更に好ましくは950℃以下とする。尚、その際の加熱時間としては、0.5～50時間程度とし、加熱処理後、5℃/分以下の速度で徐冷するのが好ましい。

【0032】本発明の層状リチウムニッケルマンガン複合酸化物粉体の製造方法は、以上の如くして製造された層状リチウムニッケルマンガン複合酸化物粉体に圧縮剪断応力を加える後処理を施すことを必須とする。

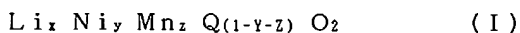
【0033】ここで、圧縮剪断応力を加える後処理とは、複合酸化物粉体粒子に圧縮及び剪断応力を負荷して粉体粒子を圧縮すると共に、その負荷応力により粉体粒子の表面の一部が削られることにより発生する微粉を粒子表面に再融着させる作用を伴う。所謂、メカノフュージョンを発現させる処理を言い、具体的には、例えば、円筒回転ドラムと、このドラム内の中心軸に固定され、先端にドラムの内周面に接する半球形状の押圧剪断ヘッドを備えた第1アームと、回転ドラムの回転前方に所定角度を隔てて中心軸に固定され、先端にドラムの内周面に接する鋭角状の爪を備えた第2アームとで構成された処理装置を用いて処理がなされる。

【0034】本発明において、この処理に用いられる処理装置としては、例えば、ホソカワケミカル社より市販されている「AM-15F」、「AF-20FS」、「AM-35F」、「AM-60F」、「AM-80F」、「AM-110F」等が挙げられる。

【0035】本発明の層状リチウムニッケルマンガン複合酸化物粉体の製造方法における層状リチウムニッケルマンガン複合酸化物は、下記一般式(I)で表される複合酸化物であるのが好ましい。

【0036】

【化2】



【0037】〔式(I)中、 x は、 $0 < x \leq 1.2$ の数であり、 y 及び z はそれぞれ、 $0.7 \leq y/z \leq 9$ 、及び、 $0 \leq 1-y-z \leq 0.5$ の関係を満たす数であり、 Q は、 Mg 、 Al 、 Ca 、 Fe 、及び Co からなる群から選択されるいずれかの金属原子を示す。〕

【0038】前記式(I)において、 $0 < x \leq 1.1$ であるのが好ましく、 x が前記範囲超過では、層状複合酸化物として結晶構造が不安定となり、電池に用いたときに電池容量の低下を引き起こす傾向となる。又、 $0.8 \leq y/z \leq 1.2$ であるのが好ましく、 $0.9 \leq y/z \leq 1.1$ であるのが更に好ましく、 $0.95 \leq y/z \leq 1.05$ であるのが特に好ましい。 y/z が前記範囲未満では、層状複合酸化物を単一相で得ることが困難な傾向となり、一方、前記範囲超過では、経済性の面で不利となる。又、 $0 \leq 1-y-z \leq 0.35$ であるのが好ましく、 $0 \leq 1-y-z \leq 0.25$ であるのが更に好ましい。 $1-y-z$ が前記範囲超過では、電池に用いたときに電池容量の低下を引き起こす傾向となる。

【0039】又、本発明の層状リチウムニッケルマンガン複合酸化物粉体の製造方法による層状リチウムニッケルマンガン複合酸化物粉体は、レーザー回折/散乱式粒度分布測定装置により測定した値として、平均一次粒子

径が、通常 $0.01 \mu\text{m}$ 以上、好ましくは $0.02 \mu\text{m}$ 以上、更に好ましくは $0.1 \mu\text{m}$ 以上であり、通常 $30 \mu\text{m}$ 以下、好ましくは $5 \mu\text{m}$ 以下、更に好ましくは $25 \mu\text{m}$ 以下のものである。又、平均二次粒子径が、通常 $1 \mu\text{m}$ 以上、好ましくは $4 \mu\text{m}$ 以上であり、通常 $50 \mu\text{m}$ 以下、好ましくは $40 \mu\text{m}$ 以下のものである。又、BET法による比表面積が、通常 $0.1 \text{m}^2/\text{g}$ 以上、好ましくは $4.0 \text{m}^2/\text{g}$ 以上であり、通常 $10.0 \text{m}^2/\text{g}$ 以下、好ましくは $8.0 \text{m}^2/\text{g}$ 以下のものである。

【0040】又、本発明の層状リチウムニッケルマンガン複合酸化物粉体の製造方法による層状リチウムニッケルマンガン複合酸化物粉体は、粉体充填密度としての200回タップ後のタップ密度が、好ましくは 0.8g/cc 以上、更に好ましくは 1.0g/cc 以上であり、好ましくは 3.0g/cc 以下、更に好ましくは 2.5g/cc 以下のものである。そして、そのタップ密度の圧縮剪断処理前のタップ密度に対する比が、好ましくは1.10以上、更に好ましくは1.15以上となって、嵩密度における顕著な改良効果を示すものとなる。尚、この比が大きい程、改良効果が顕著となるが、実用的には1.0以下、特に0.5以下である。

【0041】本発明の層状リチウムニッケルマンガン複合酸化物粉体の製造方法による層状リチウムニッケルマンガン複合酸化物粉体は、高嵩密度を有することから、リチウム二次電池の正極活物質として用いるに好適である。

【0042】本発明の製造方法により得られる層状リチウムニッケルマンガン複合酸化物粉体のリチウム二次電池の正極活物質としての使用法は、従来公知の方法による。即ち、正極活物質としての本発明の層状リチウムニッケルマンガン複合酸化物粉体を、結着剤と共に、必要に応じて導電剤を加え、溶媒に分散させた塗布液となし、該塗布液を集電体表面に塗布し、乾燥させた後、好ましくは一軸プレスやロールプレス等により圧密化処理を行うことにより、集電体表面に正極活物質含有層を形成し、正極とされる。

【0043】ここで、用いられる結着剤としては、例えば、ポリビニリデンフルオライド、ポリテトラフルオロエチレン、ポリメチルメタクリレート、ポリエチレン等の樹脂、スチレンブタジエンゴム、アクリロニトリルブタジエンゴム、エチレンプロピレンゴム、弗素ゴム等のゴム、その他、ポリ酢酸ビニル、セルロース等の高分子物質が、又、導電剤としては、例えば、天然黒鉛、人造黒鉛等の黒鉛、アセチレンブラック等のカーボンブラック、ニードルコークス等の無定形炭素等の炭素質微粒子が、それぞれ挙げられ、又、溶媒としては、例えば、エチレンオキシド、テトラヒドロフラン等のエーテル系溶媒、メチルエチルケトン、シクロヘキサノン等のケトン系溶媒、酢酸メチル、アクリル酸メチル等のエステル系溶媒、ジエチルトリアミン、 N 、 N -ジメチルアミノア

ロピルアミン等のアミン系溶媒、N-メチルピロリドン、ジメチルホルムアミド、ジメチルアセトアミド等の非プロトン性極性溶媒等が挙げられる。

【0044】又、集電体としては、アルミニウム、ステンレス鋼、ニッケルメッキ鋼等の、厚みが、通常1~1000 μ m、好ましくは5~500 μ mの箔が挙げられ、正極の集電体としてはアルミニウム箔が好ましい。尚、正極活物質含有層の厚みは、通常1~1000 μ m、好ましくは10~200 μ mとされる。

【0045】又、正極活物質含有層における正極活物質の含有割合は、電池容量等の電池特性を確保する上で、通常10重量%以上、好ましくは30重量%以上、更に好ましくは50重量%以上とし、電極としての機械的強度等を確保する上で、通常99.9重量%以下、好ましくは99重量%以下、更に好ましくは95重量%以下とする。又、結着剤の含有割合は、電極としての機械的強度等を確保する上で、通常0.1重量%以上、好ましくは1重量%以上、更に好ましくは5重量%以上とし、電池容量や導電性等の電池特性を確保する上で、通常80重量%以下、好ましくは60重量%以下、更に好ましくは40重量%以下とする。又、導電剤の含有割合は、導電性等の電池特性を確保する上で、通常0.01重量%以上、好ましくは0.1重量%以上、更に好ましくは1重量%以上とし、電池容量等の電池特性を確保する上で、通常50重量%以下、好ましくは30重量%以下、更に好ましくは15重量%以下とする。

【0046】又、負極は、負極活物質を、結着剤と共に溶媒に分散させた塗布液となし、該塗布液を集電体表面に塗布し、乾燥させた後、好ましくは一軸プレスやロールプレス等により圧密処理を行うことにより、集電体表面に負極活物質含有層を形成し、負極とされる。

【0047】ここで、用いられる負極活物質としては、例えば、リチウム、リチウムアルミニウム合金、黒鉛、石炭系や石油系コークスの炭化物、石炭系や石油系ピッチの炭化物、ニードルコークス、ピッチコークス、フェノール樹脂や結晶セルロース等の炭化物、ファーネスブラックやアセチレンブラック等のカーボンブラック、及び、 SnO 、 SnO_2 、 $\text{Sn}_{1-x}\text{M}_x\text{O}$ (MはHg、P、B、Si、Ge、又はSbであり、 x は $0 \leq x < 1$ である。)、 $\text{Sn}_3\text{O}_2(\text{OH})_2$ 、 $\text{Sn}_{3-x}\text{M}_x\text{O}_2(\text{OH})_2$ (MはMg、P、B、Si、Ge、Sb、又はMnであり、 x は $0 \leq x < 3$ である。)、 LiSiO_2 、 SiO_2 、 LiSnO_2 等が挙げられ、又、結着剤、溶媒等は前記正極の形成における同様のものが挙げられる。又、集電体としては、銅、ニッケル、ステンレス鋼、ニッケルメッキ鋼等の箔が挙げられ、負極の集電体としては銅箔が好ましい。

【0048】そして、集電体表面に正極活物質含有層を有する正極と、集電体表面に負極活物質含有層を有する負極と、電解質層と、必要に応じて正極と負極の間に介

在させるセパレータとから、リチウム二次電池が構成される。

【0049】ここで、電解質層としては、例えば、電解質を溶媒に溶解させた有機電解液、又は、高分子固体電解質、ゲル状電解質、無機固体電解質等が用いられ、中で、有機電解液が好ましい。

【0050】その有機電解液における電解質としては、例えば、 LiCl 、 LiBr 、 LiClO_4 、 LiAsF_6 、 LiPF_6 、 LiBF_4 、 $\text{LiB}(\text{C}_6\text{H}_5)_4$ 、 LiCH_3SO_3 、 LiCF_3SO_3 、 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ 、 $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ 、 $\text{LiN}(\text{SO}_3\text{CF}_3)_2$ 、 $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ 等が挙げられ、又、溶媒としては、例えば、ジエチルエーテル、1,2-ジメトキシエタン、1,2-ジエトキシエタン、テトラヒドロフラン、2-メチルテトラヒドロフラン、1,4-ジオキサン、1,3-ジオキソラン等のエーテル類、4-メチル-2-ペンタノン等のケトン類、メチルホルメート、メチルアセテート、メチルプロピオネート等のエステル類、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネート、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート、ビニレンカーボネート等のカーボネート類、 γ -ブチロラクトン、 γ -バレロラクトン等のラクトン類、1,2-ジクロロエタン等のハロゲン化炭化水素類、スルホラン、メチルスルホラン等のスルホラン系化合物類、アセトニトリル、プロピオニトリル、ブチロニトリル、バレロニトリル、ベンゾニトリル等のニトリル類、ジエチルアミン、エチレンジアミン、トリエタノールアミン等のアミン類、リン酸トリメチル、リン酸トリエチル等のリン酸エステル類、N,N-ジメチルホルムアミド、N-メチルピロリドン、ジメチルスルホキシド等の非プロトン性極性溶媒等が挙げられる。

【0051】又、セパレータとしては、ポリエチレン、ポリプロピレン等のポリオレフィン、ポリビニリデンフルオライド、ポリテトラフルオロエチレン、ポリエステル、ポリアミド、ポリスルホン、ポリアクリロニトリル、セルロース、セルロースアセテート等の高分子の微多孔性フィルムが用いられる。

【0052】

【実施例】以下、本発明を実施例によりさらに具体的に説明するが、本発明はその要旨を越えない限り以下の実施例に限定されるものではない。

【0053】比較例1

リチウム源化合物としての水酸化リチウム-水塩 ($\text{LiOH} \cdot \text{H}_2\text{O}$) と、ニッケル源化合物としての水酸化ニッケル ($\text{Ni}(\text{OH})_2$) と、マンガン源化合物としての三二酸化マンガン (Mn_2O_3) とを、最終的に得られる層状リチウムニッケルマンガン複合酸化物における各原子のモル比で、リチウム原子 [Li] : ニッケル原

11

子〔Ni〕：マンガン原子〔Mn〕＝1.05：0.50：0.50となる量を、純水に加えて固形分濃度12.5重量%のスラリーを調製し、このスラリーを、循環式媒体攪拌型湿式粉碎機（シンマルエンタープライゼス社製「ダイノミルKD-20B型」）を用いて混合すると共に、スラリー中の各化合物の平均粒子径が、レーザー回折／散乱式粒度分布測定装置により測定した値として0.3 μ mになるまで、約6時間湿式粉碎した。このスラリーの粘度は、BM型粘度計により測定した値として290mPa・秒であった。

【0054】次いで、得られたスラリーを、スプレードライヤー（藤崎電機社製「四流体ノズル型スプレードライヤー」）を用いて、23m³/分の導入量でダウンフローさせた90℃の加熱空気流に対して直交方向に、加圧空気により300m/秒の線速でノズルから噴出させ、噴霧乾燥により乾燥させた後、得られた粉体粒子を空气中で900℃で10時間焼成することにより、モル比で、リチウム原子〔Li〕：ニッケル原子〔Ni〕：マンガン原子〔Mn〕＝1.05：0.50：0.50の層状リチウムニッケルマンガン複合酸化物粉体を製造した。

【0055】得られた層状リチウムニッケルマンガン複合酸化物粉体は、ほぼ球形を有する粒子であり、粉末X線回折を測定したところ、菱面体晶の層状リチウムニッケルマンガン複合酸化物であることが確認された。又、全自動粉体比表面積測定装置（大倉理研製「AMS8000型」）を用いてBET法による比表面積を測定したところ、6.14m²/gであった。又、得られた複合酸化物粉体の約5gを10mlのガラス製メスシリンダーに入れ、200回タップした後の粉体充填密度をタップ密度として測定したところ、1.12g/ccであった。

【0056】実施例1

比較例1で得られた層状リチウムニッケルマンガン複合酸化物粉体の約300gを採取し、ホソカワケミカル社製「AM-20FS」を用いて、インナーピースの回転数を2000rpmとして10分間、圧縮剪断応力を与えることにより後処理を施した。

【0057】得られた層状リチウムニッケルマンガン複

12

合酸化物粉体は、ほぼ球形を有する粒子であり、粉末X線回折を測定したところ、菱面体晶の層状リチウムニッケルマンガン複合酸化物であることが確認された。

【0058】又、比較例1における同様の方法で比表面積を測定したところ、9.27m²/gであった。

又、得られた複合酸化物粉体の約5gを10mlのガラス製メスシリンダーに入れ、200回タップした後の粉体充填密度をタップ密度として測定したところ、1.49g/ccであり、比較例1における粉碎前のタップ密度に対する比は1.33であった。

【0059】応用例

前記比較例1及び実施例1で得られた層状リチウムニッケルマンガン複合酸化物粉体、導電剤としてのアセチレンブラック、及び、結着剤としてのポリテトラフルオロエチレン粉体を、75重量%：20重量%：5重量%の割合となる量で混合し、直径9mmの円形に打ち抜いたときの重量が約8mgとなる厚さでシートに成形し、該シートから直径9mmの円形に打ち抜き、アルミニウム製エキスパンドメタルの片面に圧着することにより正極を作製した。この正極を試験極とし、リチウム金属を対極としてコインセルを組み、これに、電流密度0.2mA/cm²の定電流充電、即ち正極からリチウムイオンを放出させる反応を上限4.3Vで行い、次いで、電流密度0.2mA/cm²の定電流放電、即ち正極にリチウムイオンを吸蔵させる反応を下限3.0Vで行ったときの、正極活物質単位重量当たりの初期充電容量〔Qs(C) (mAh/g)〕、及び、初期放電容量〔Qs(D) (mAh/g)〕を測定した。その初期放電容量〔Qs(D) (mAh/g)〕を、電流密度11mA/cm²で測定した放電容量〔Qa(D) (mAh/g)〕と共に、表1に示した。

【0060】又、それらの初期放電容量〔Qs(D) (mAh/g)〕、及び放電容量〔Qa(D) (mAh/g)〕を、前記タップ密度から単位容積あたりに換算し、初期放電容量〔Qs'(D) (mAh/cc)〕、及び放電容量〔Qa'(D) (mAh/cc)〕として表1に併記した。

【0061】

【表1】

13
表1

14

	比較例1の 複合酸化物粉体	実施例1の 複合酸化物粉体
正極		
初期放電容量[Qs(D)] (mAh/g)	146.1	141.0
初期放電容量[Qs'(D)] (mAh/cc)	163.6	210.1
at 電流密度0.2mA/cm ²		
放電容量[Qa(D)] (mAh/g)	91.88	80.15
放電容量[Qa'(D)] (mAh/cc)	102.9	119.4
at 電流密度11mA/cm ²		

【0062】以上の比較例1と実施例1の結果から、本発明の製造方法により得られる実施例1の層状リチウムニッケルマンガン複合酸化物粉体は、比較例1の層状複合酸化物に対する嵩密度の改良効果が大きく、高嵩密度を有することが明らかであり、更に、応用例の結果から、本発明の製造方法により得られる実施例1の層状リチウムニッケルマンガン複合酸化物粉体を正極活物質として用いたリチウム二次電池は、比較例1の層状複合酸化物を正極活物質として用いた場合に比して、単位重量*

* 当たりで同等の電池特性を有し、圧縮剪断処理による電池特性上の劣化等を生じてはいないことが明らかであり、従って、単位容積当たりの電池特性において優れることが明らかである。

【0063】

【発明の効果】本発明によれば、高嵩密度を有し、リチウム二次電池の正極活物質として用いるに好適な層状リチウムニッケルマンガン複合酸化物粉体を製造する方法を提供することができる。

フロントページの続き

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